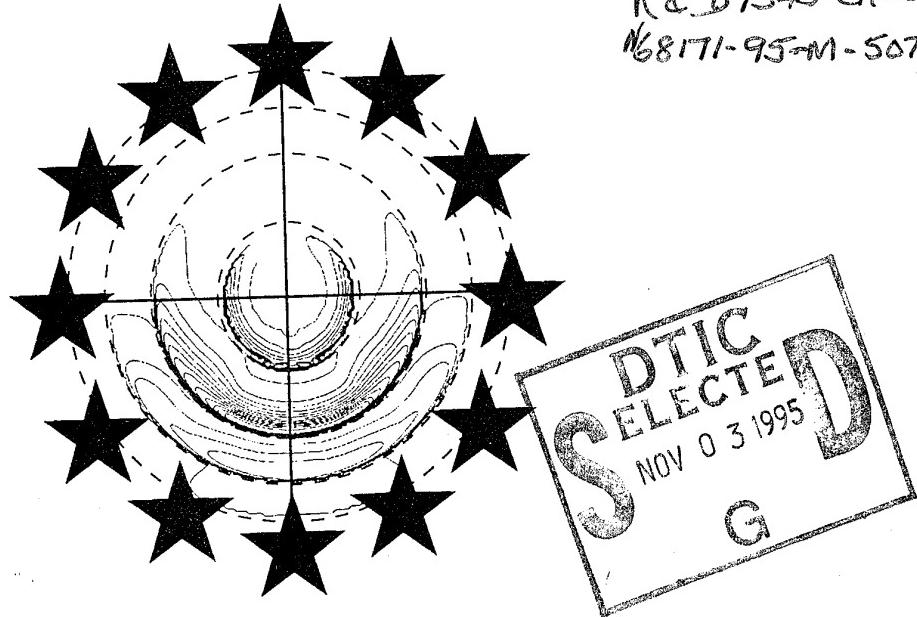


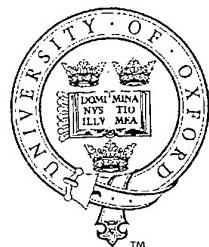
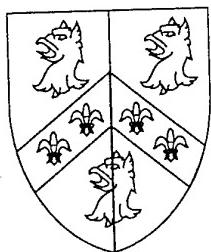
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MOLECULAR SPECTROSCOPY PHOTON INDUCED DYNAMICS

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**EIGHTH
EUROPEAN
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3RD - 7TH SEPTEMBER 1995

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EIGHTH EUROPEAN WORKSHOP ON MOLECULAR SPECTROSCOPY
AND PHOTON-INDUCED DYNAMICS

3rd - 7th September 1995

at

Trinity College, Oxford
The Physical and Theoretical Chemistry Laboratory
and
Rutherford Appleton Laboratory.

Final announcement and programme

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Address for all correspondence:

8th European Workshop,
Physical and Theoretical Chemistry Laboratory,
South Parks Road,
OXFORD OX1 3QZ
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WELCOME

It is a great pleasure to welcome all participants to this Eighth European Workshop on Molecular Spectroscopy and Photon Induced Dynamics, to Oxford and to Trinity College. We hope that this will be a very enjoyable and scientifically rewarding meeting for all of us. In the tradition of these conferences there is a wide range of topics, including some exciting new advances. Molecular spectroscopy and dynamics continues to provide spectacular progress in physical chemistry, despite its apparent maturity. Many advances have been reported at the previous Workshops; the list gives an idea of their truly international and European character:

Maria Laach, Germany, 1979
De Eemhof, The Netherlands, 1982
Seillac, France, 1985
Oxford, England, 1987
Wegimont, Belgium, 1989
Barcelona, Spain, 1991
Maratea, Italy, 1993
Oxford, England, 1995.

Long may the series continue !

EIGHTH EUROPEAN WORKSHOP

PROGRAMME

PROGRAMME

Sunday 3/9/95

6-8 pm Registration at Trinity College. A buffet supper will be available from 6.30 pm.

Monday 4/9/95

7.45 am ***** breakfast in Trinity *****

9.30-11 Registration and coffee in the PTCL

11 am Opening ceremony-- Prof. J.P. Simons

Session 1: *Photon-induced dynamics in the gas phase*

Chairman: Prof. J.P. Simons

11.15 Prof. C. Wittig, "The photophysics and photochemistry of NO_3 "

12.00 Dr. J. Vigué, "Spectroscopy and photodissociation of oriented molecules"

1 pm ***** LUNCH *****

Session 2: *More photon-induced dynamics*

Chairman: Dr. G. Hancock

2.30 Dr. H. Bitto, "Intersystem crossing studied by high resolution
quantum beat spectroscopy"

3.15 Prof. R.J. Gordon, "Coherent control of unimolecular reactions"

4.00 ***** tea *****

4.30 Dr. D.E. Manolopoulos, "Quantum and semiclassical theories for photodissociation"

5.15 Prof. A. Kupperman, "A strong geometric phase resonance in the
 $H + D_2 = HD + D$ reaction"

6.00 Prof. M.N.R. Ashfold, "High resolution photofragment translational spectroscopy"

7.00 ***** DINNER *****

8.30 First Poster session: Group A.

Tuesday 5/9/95

7.45 am **** Breakfast ***

Session 3: Spectroscopy and photon-induced dynamics at interfaces

Chairman: Dr. H. Lefevre-Brion

9.00 Prof. P. Guyot-Sionnest, "Vibrational surface dynamics"
9.45 Dr. C.D. Bain, "Structure and phase transitions of monolayers of n-alcohols on water"
10.30 ***** Coffee ***

Session 4: Photon-induced processes in extraterrestrial environments

Chairman: Prof. J. Rostas

11.00 Prof. J.P. Maier, "Spectroscopy of carbon chains of relevance to astrophysics"
11.45 Dr. J. Tennyson, "Infrared observations of the impact
of comet Shoemaker-Levy-9 with Jupiter"

1 pm ***** LUNCH *****

2.30 College tours, punting etc.

7.00 ***** DINNER *****

8.30 Second Poster session-Group B

Wednesday 6/9/95

7.45 am **** Breakfast ***

8.45 Coaches depart for RAL

Session 5: Photon-induced processes and spectroscopy in the VUV

Chairman: Dr. J.H.D. Eland

9.15 Prof. C. deLange, "Laser photoelectron spectroscopy: chemistry with a light touch"
10.00 Dr. F. Penent, "Double photoionization processes studied by
threshold photoelectrons coincidence"
10.45 ***** Coffee ***
11.00 Dr. F. Heiser, "Fragmentation dynamics of core-excited molecules"

Session 6: Atoms and molecules in intense fields

Chairman: Dr. T.P. Softley

11.45 Dr. B. Friedrich, "Polarisation of molecules by non-resonant laser fields"
12.30 Prof. M.H.R. Hutchinson, "The interaction of atoms and molecules
with intense laser radiation"
1.15 pm ***** LUNCH *****

Wednesday (cont.)

2.15 *Introduction to the Central Laser Facility* - Prof. Mike Key
2.45 Tour of the central laser facility

4.00 ***** tea *****
4.30 Coaches leave RAL for Oxford

7.00 ***** DINNER *****

8.30 Bar open for informal discussions

Thursday 7/9/95

7.45 am ***** Breakfast *****

Session 7: Spectroscopy and dynamics in van der Waals complexes and clusters

Chairman: Dr. M. Gonzalez

9.00 Dr. P.M. Felker, "Species-selective studies of intramolecular resonances
 in molecular clusters by non-linear Raman spectroscopy"
9.45 Dr. G. Delgado-Barrio, "Competitive internal transfers in metastable decay
 of cluster ions"
10.30 ***** coffee *****
11.00 Dr. C. Jouvet, "Time evolution in van der Waals reactive clusters"
11.45 Dr. B. von Issendorf, "Optical spectroscopy of ionized rare gas clusters"
1 pm ***** LUNCH *****

Session 8: Photon-induced processes and molecular spectroscopy in condensed phases

Chairman: Prof. A. Beswick

2.30 Prof. J. Schmidt, "Single molecule magnetic resonance spectroscopy"
3.15 Prof. J. Knoester, "Collective optical properties of molecular assemblies"
4.00 ***** tea *****
4.30 Dr. N. Schwentner, "Towards an understanding of elementary photochemical reactions
 in condensed phases"
5.15 Dr. D. Klug, "Relaxation dynamics in proteins studied by ultrafast spectroscopy"

6.00 *Closing remarks* - Prof. V. Aquilanti.

7.30 ***** CONFERENCE BANQUET *****

EIGHTH EUROPEAN WORKSHOP

**INVITED
LECTURES**

THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF NO₃

C.W. Riehn, K. Mikhaylichenko, L. Valachovic and C. Wittig

Department of Chemistry
University of Southern California
Los Angeles, California 90089-0482
U.S.A.

Though the NO₃ radical absorbs strongly throughout the visible and near infrared ($E' \leftarrow A_2'$; $\sigma = 2 \times 10^{-17} \text{ cm}^2$ at 662 nm), its spontaneous emission life-times exceed 100 μs because of couplings between the E' state and one or more lower electronic states. A strong vibronic interaction is apparent in the origin region and can be assigned to pseudo-Jahn-Teller interactions of E' with E'' and/or A₂'. Weaker interactions are also present, resulting in a complicated spectrum. Since rotations are cooled to only 6K, the LIF spectra are hopelessly congested and when reactive channels are open (below), there will be considerable averaging, washing out state-to-state fluctuations in rates. As the photon energy is increased, unimolecular reactions commence, first via (i) the NO + O₂ channel, and at slightly higher energies also via (ii) the O + NO₂ channel. Since (i) involves a tight transition state, tunneling can occur. At energies above the classical barrier but below the opening of the O + NO₂ channel, k(E) rises from 1×10^9 to 5×10^9 over a range of $\sim 200 \text{ cm}^{-1}$, and can be fitted by using RRKM theory. Below this barrier, k(E) varies much more rapidly with energy, changing by two orders of magnitude in less than 100 cm^{-1} (i.e., from 3×10^7 to 3×10^5). These slow rates may be due, at least in part, to tunneling. Measurements of c.m. kinetic energies indicate that O₂ is formed in the ${}^1\Delta$ state throughout nearly all of this range, with the ${}^3\Sigma$ ground state produced at only the smallest k(E) values. When the O + NO₂ channel opens, there are a number of competing processes. Reaction via the ground state A₂' surface can account for rapid dominance of the O + NO₂ channel as the energy increases, but not to the extent observed. Moreover, if reaction is fast enough to follow the zeroth-order E' surface, the O + NO₂ channel will dominate, but to a greater extent than what is observed. Vibronic interactions control the access routes to these competing channels.

SPECTROSCOPY AND PHOTODISSOCIATION OF ORIENTED MOLECULES

by A. DURAND, G. BAZALGETTE, J.C. LOISON, E. AUDOUARD, R. WHITE, G. TRENEC and J. VIGUE

Laboratoire Collisions Agrégats Réactivité, IRSAMC
Université Paul SABATIER and CNRS URA 770
118, route de NARBONNE,
31062 TOULOUSE Cedex, France

After the pioneering works of Loesch and Remscheid (1) and of Friedrich and Herschbach (2), it is possible to orient the molecular axis of polar diatomic molecules and to study the spectroscopy of the pendular states produced by a strong Stark mixing of the lowest rotational levels.

We will describe two experiments we have done here on these subjects with ICl molecules:

- we have made a detailed study of the transitions between the pendular states of the A and X electronic levels of ICl. By a careful simulation and assignment of the numerous hyperfine lines, we have shown that the dipole moments of the A and X states have the same sign (3). This result contradicts the previous works (2,4), but it is supported by an other experiment (5) and it is also easily explained by elementary quantum chemistry. We have also measured the dipole moment in the A state as a function of the vibrational level with great accuracy: this variation exhibits very clearly the transition from ionic to covalent nature when the molecule reaches dissociation.

- we have produced an oriented molecular beam of ICl, by applying an intense electric field on a rotationally cold beam (ICl seeded in argon). The oriented molecules have been photodissociated and we have detected the iodine atoms recoiling in the direction of the electric field. This experiment measures directly the large orientation of the molecular axis, and it also gives a direct access to the sign of the dipole moment of ICl in its ground X state, found to be $I^+ Cl^-$. This is a new and simple way of measuring the sign of a dipole moment.

Acknowledgements: Financial support by Région Midi-Pyrénées is gratefully acknowledged.

References:

- 1 -H.J. LOESCH and A. REMSCHEID, J. Chem. Phys. 1990, **93**, 4779
- 2 -B. FRIEDRICH and D.R. HERSCHBACH, Nature 1991, **353**, 412
- 3 -A. DURAND, J.C. LOISON and J. VIGUE, J. Chem. Phys. 1994, **101**, 3514
- 4 -B. FRIEDRICH et al, J.C.S. Faraday Trans. 1993, **89**, 1539
- 5 -B. FRIEDRICH, A. SLENCZKA and D. HERSCHBACH, Chem. Phys. Lett. 1994, **221**, 333
- 6 -G. BAZALGETTE et al , submitted to Chem. Phys. Lett.

Intersystem Crossing Studied by High-Resolution Quantum Beat Spectroscopy

H. Bitto

Physikalisch-Chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich,
Switzerland

The dynamics of polyatomic molecules in electronically excited states may be studied by spectroscopic methods in both the frequency and the time domain. Quantum beat spectroscopy, a time domain method, has proven to be very powerful for investigating the dynamics in the intermediate coupling case since coherently excited states can be investigated with lifetime-limited resolution. We have applied this method using clean coherent excitation with near Fourier transform-limited nanosecond laser pulses to assess the dynamics and underlying mechanisms of rovibronic singlet states interacting with background triplet states.

In the first part, the characterization of molecular eigenstates by quantum beat spectroscopy is illustrated. In the 1B_2 electronic state of ${}^{12/13}CS_2$ the eigenstates are resolved with our laser bandwidth allowing us to determine their lifetimes, Landé g factors and hyperfine splittings. Based on these properties and the eigenstate density a coupling scheme of the involved states is proposed.

In the second part, time domain spectroscopy is applied to coherently excited eigenstates for the determination of state densities and average lifetimes. These parameters allow us to study the effects of rotation, internal rotation, and molecular symmetry on the intersystem crossing dynamics in carbonyl and heterocyclic aromatic compounds and their methyl substituted species. Furthermore, quantum beats of rovibronic states with rotational quantum numbers $N \leq 1$ show that hyperfine interaction must be considered to understand the S_1 dynamics on the microsecond time scale.

Coherent Control of Unimolecular Reactions

Langchi Zhu, Valeria Kleiman, Xiaonong Li, and Robert J. Gordon
Department of Chemistry (m/c 111)
University of Illinois at Chicago

We have used the Brumer-Shapiro method of quantum mechanical interference to control the ionization rates of H₂S and HI. In these experiments molecules were excited simultaneously with three UV photons of frequency ω_1 , and one VUV photon of frequency ω_3 , where ω_3 was produced by third harmonic generation from ω_1 in Xe. Product ions were observed to vary sinusoidally as the phase difference between the two laser beams was increased. In the case of H₂S, the H₂S⁺, HS⁺, and S⁺ ion signals were all in phase. Laser intensity measurements showed that HS⁺ and S⁺ were produced by fragmentation of the parent H₂S⁺ ion. In the case of HI, we found that in some energy regions the I⁺ signal lagged the HI⁺ signal by 150±30°. The most plausible explanation of our data is that HI⁺ is produced by autoionization, while I atoms are produced by predissociation of HI, and are subsequently ionized by absorption of additional photons. We have demonstrated for the first time coherent control of the total cross section for bound-to-continuum transitions. We have further shown that it is possible to control the product branching ratio by varying the phase difference between two laser beams.

Quantum and Semiclassical Theories for Photodissociation

David E Manolopoulos

University of Nottingham

The anion photoelectron spectroscopy (or ‘transition state spectroscopy’) experiments of Neumark and coworkers have been one of the most exciting developments in molecular photodissociation in recent years. In favourable circumstances, when the equilibrium geometry of the anion lies close to the neutral transition state, the photoelectron spectrum of the anion can provide a direct, vibrationally resolved picture of the neutral reaction dynamics in the transition state region that can be interpreted with the aid of the Franck-Condon principle. These experiments have therefore attracted a great deal of theoretical attention, not least because they can be simulated through the calculation of a comparatively simple total absorption spectrum. This is the most averaged quantity that it is possible to calculate for a molecular photodissociation process, requiring neither photofragment state nor angular resolution. Because of this, there are a number of very simple theories for calculating total absorption spectra, both quantum mechanically and semiclassically. These theories will be reviewed in this talk, following a brief discussion of our own work on understanding the dynamics of the F+H₂ reaction through a study of the FH₂⁻ photoelectron spectrum. In particular, the emphasis of the talk will be on which of the available theories are likely to prove most useful for studying the photoelectron spectra of the more complex tetratomic anions like H₃O⁻ and H₂O₂⁻ that have recently been measured experimentally.

Abstract of paper to be presented at the Eighth European Workshop on
Molecular Spectroscopy and Photon Induced Dynamics
University of Oxford, England 3-7 September 1995

A Strong Geometric Phase Resonance in the
 $H + D_2 \rightarrow HD + D$ Reaction

Aron Kuppermann and Yi-Shuen Mark Wu
California Institute of Technology
Pasadena, CA 91125

Three-dimensional accurate quantum mechanical calculations of the differential cross section, timedelay and collision lifetime of the $H + D_2(v,j) \rightarrow HD(v',j') + D$ reaction show that the $v=j=v'=0, j'=4$ and 5 transitions display pronounced resonances in the total energy range of 1.47 eV to 1.53 eV, if the geometric phase is included, but not otherwise. No other open channels display pronounced resonances in this range. Their width is in the 20 meV to 40 meV range and their duration lies between 68 fs and 164 fs, which is long compared with internal motion times of 8 fs to 10 fs or rotation times of 2 fs to 11 fs. Experiments capable of verifying these predictions are discussed.

References:

1. Y.-S. M. Wu, A. Kuppermann and B. Lepetit, *Chem. Phys. Lett.*, **186**, 319 (1991)
2. Y.-S. M. Wu, A. Kuppermann, *Chem. Phys. Lett.*, **201**, 178 (1993)
3. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.*, **205**, 577 (1993); erratum **213**, 636 (1993)
4. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.*, in press

HIGH RESOLUTION PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

M.N.R. Ashfold

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

The technique of H atom photofragment translational spectroscopy (PTS), pioneered by Welge and coworkers at Universität Bielefeld, has been used in Bristol to investigate further details of the near ultraviolet photodissociation of the molecules NH₃, PH₃, H₂S, CH₃SH, CH₃NH₂, C₂H₂ and the radical species, CH₃, and the Lyman- α photolysis of H₂O, H₂S, HCN and CH₄ [1]. In each case the structure evident in the H atom time-of-flight (TOF) spectrum has provided new, detailed information about the energy disposal in the partner molecular fragment and thus about the dynamics of the primary photodissociation process. The following examples will be considered in some detail:

(i) Near UV photolysis of C₂H₂, C₂HD and C₂D₂ [2]. These will serve to demonstrate the superb resolution that is available with the technique. This study allows detailed determination of the rotational and vibrational energy disposal in the partner C₂H(C₂D) fragments, as a function of parent vibronic state and provides some of the clearest clues yet as to the detailed dynamics of this fragmentation process. It also sets to rest any lingering controversy concerning the magnitude of D₀(H-CCH).

(ii) Near UV photolysis of NH₃, NH₂D, NHD₂ and ND₃ [3]. The latest H atom PTS studies of this model system serve to quantify the striking correlation between the recoil velocities (as viewed via the H atom product) and the rotational angular momentum of the partner NH₂ partner. The 'partial' anisotropy parameters, $\beta|v,N\rangle$, so derived confirm that the H atoms formed in association with the least rotationally excited products recoil in the plane of the excited (D_{3h}) molecule, whereas those that partner NH₂ fragments with the highest levels of *a*-axis rotational excitation are ejected perpendicular to this plane (*i.e.* parallel to the C₃ top axis). Studies of the mixed isotopomers highlight the (hitherto largely unrecognised) contribution made by internal conversion (to high levels of the ground electronic state) to the overall dissociation yield.

(iii) Near UV photolysis of the CH₃ radical [4]. A seeded beam of methyl radicals was produced by pulsed pyrolysis of azomethane and photodissociated at *ca.* 216 nm, the origin of the intense but predissociated $\tilde{B} - \tilde{X}$ absorption system of CH₃. TOF analysis of the resulting H atoms shows the parther CH₂ fragments to be formed predominantly (if not exclusively) in the vibrationless level of the first excited singlet ($\tilde{\alpha}^1A_1$) electronic state.

References

1. For a comprehensive review, see: M.N.R. Ashfold, D.H. Mordaunt and S.H.S. Wilson, in *Advances in Photochemistry* (D. Neckers, D. Volman and G. von Bunau, eds.), 1995, **21**, (in press)
2. D.H. Mordaunt and M.N.R. Ashfold, *J. Chem. Phys.* (1994), **101**, 2630; S.H.S. Wilson, C.L. Reed, D.H. Mordaunt, M.N.R. Ashfold and M. Kawasaki, *Bull. Chem. Soc. Japan* (submitted).
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VIBRATIONAL SURFACE DYNAMICS

P. Guyot-Sionnest

James Franck Institute, University of Chicago, Chicago, USA

Time-resolved nonlinear spectroscopy at surfaces is used to monitor vibrational energy transfer and phase relaxation of molecular vibrations of adsorbates.

The hydrogenated Silicon surfaces is an example of system where both energy and phase relaxation are mostly due to phonon-vibration coupling. Several experiments have specifically addressed the dynamics of the stretching mode of the Si-H bond for the Si(111)/H 1x1 and Si(100)/H 2x1 surfaces. Dynamics on these systems are slow, nanoseconds for energy relaxation and tens of picoseconds for phase relaxation.

CO on metallic surfaces is an example of a system where energy relaxation is primarily mediated by electron-vibration coupling. Our experiments attempt to vary the strength of this coupling by placing the interface in a very large electric field. This has the role of shifting the relative position of the Fermi level and the molecular orbitals. This is done electrochemically, since stable CO/Pt monolayer can be formed over a large potential range in nonaqueous electrolyte. Using time-resolved pump-probe sum-frequency generation with a 1.2 ps IR pulse, the relaxation of the excited CO stretching vibration is followed. Typical relaxation times of $\approx 2\text{ps}$ are measured. Preliminary data indicate a slight decrease of the lifetime as the potential is displaced negative of the potential of zero charge, consistent with theoretical predictions by Head-Gordon and Tully.

Structure and phase transitions of monolayers of n-alcohols on water

Colin Bain*, Rüdiger Braun and Brian Casson

PTCL,

University of Oxford

Sum-frequency vibrational spectroscopy (SFS) has been used to study the structure of monolayers of *n*-alcohols on the surface of water. Monolayers of medium-chain alcohols ($C_8 - C_{14}$) are known to undergo a first-order phase transition at temperatures well-above the bulk melting point. X-ray diffraction has shown that the monolayers are hexagonally packed below the transition temperature, T_m , and translationally disordered above it.¹ The effect of surface pressure on T_m has been used to deduce the change in area per molecule at the phase transition.² We have employed SFS to obtain vibrational spectra of *n*-alcohol monolayers above and below T_m . From these spectra, we can deduce an upper limit to the change in area per molecule at T_m , and observe certain types of conformational disorder associated with the phase transition. Temperature-dependent changes in the structure of the phase both above and below T_m are also clearly evident.

¹ A. Renault et al. *J. Phys. II France* **1993**, *3*, 761.

² B. Berge et al. *Phys. Rev. Lett.* **1994**, *73*, 1652.

SPECTROSCOPY OF CARBON CHAINS OF RELEVANCE TO ASTROPHYSICS

John P. Maier
Institute for Physical Chemistry
University of Basel, Switzerland

Absorption spectra of linear carbon chains, C_{2n} , C_{2n}^- and $C_{2n}H$, have been observed in 5K neon matrices in the 400-2500 nm range. These have been assigned to their $^3\Sigma - ^3\Sigma$, $^2\Pi - ^2\Pi$, and $^2\Pi - ^2\Pi$ transitions, respectively. The measurements were accomplished by mass-selected codeposition of carbon cations or anions with neon to produce the matrix. The implications of the results in connection with the suggestion that such species are good candidates for the carriers of the diffuse interstellar bands will be considered.

Infrared observations of the collision of Comet Shoemaker-Levy 9 with Jupiter

Jonathan Tennyson,

Department of Physics and Astronomy, University College London, London WC1E 6BT

During a week in July 1994 the twenty-one fragments of comet Shoemaker-Levy 9 crashed spectacularly into the planet Jupiter closely watched by the world's astronomers. The UCL group obtained both spectra and images of the collision and its aftermath using two infrared telescopes (NASA's IRTF [1] and UKIRT) situated on top of Mauna Kea in Hawaii.

The collisions resulted in the biggest explosions ever witnessed in our solar system. Infrared wavelengths proved to be very sensitive both to the immediate collision and its long term aftermath (the scars are still clearly visible). The talk will present images available from a number of telescopes but will concentrate on the results extracted from our own observations.

Prior to the collision we had been monitoring auroral activity in Jupiter ionosphere using infrared emissions of the H_3^+ molecular ion (eg [2]). The impacts caused an marked brightening in the H_3^+ emissions. However larger explosions, such as the one caused by the third impact (C), caused huge quantities of hot methane to be thrown into the ionosphere over a very extended region [3]. Monitoring methane emissions gives light curves, temperature information and a handle on the amount of energy dissipated in the infrared.

Observations of H_3^+ in the Jovian auroral regions both during and after the impacts gave a number of interesting and unexpected results. For instance, about a week after the of the impacts, which all took place along latitude 44° South, the southern aurora dimmed very significantly. Perhaps even more surprisingly the northern aurora was found to be up to five times as bright as normal. This unusual situation lasted for approximately a week before normality returned [4].

It would appear that the southern aurora was disrupted by dust and other particulate matter thrown up by the cometary impacts. The week time lag implies a north-south wind speed of about 70 kilometres per hour, a figure entirely unknown before the impacts but in agreement with estimates obtained from direct observation of the impact scars by the Hubble Space Telescope. This dust not only impeded the flow of charged particles into the south, but increased the electrical resistance leading to an increase in the current flowing into the north and a consequent increase in northern auroral activity.

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2. R. Baron, R.D. Joseph, T. Owen, J. Tennyson, S. Miller and G.E. Ballester, Imaging Jupiter's aurorae from H_3^+ emissions in the 3–4 μm band, *Nature*, **353**, 539 (1991).
3. B.M. Dinelli, N. Achilleos, H.A. Lam, J. Tennyson, S. Miller, M.-F. Jagod, T. Oka and T.R. Geballe, Infrared spectroscopic studies of the impact of fragment C of SL9, in *Proceedings of European SL-9/Jupiter Workshop*, R. West and H. Böhnhardt (eds.), 245–249 (ESO, Garching, 1995).
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Laser photoelectron spectroscopy: chemistry with a light touch

C.A. de Lange
University of Amsterdam
Laboratory for Physical Chemistry
Nieuwe Achtergracht 127
1018 WS Amsterdam
The Netherlands

Resonance enhanced multiphoton ionization in combination with high-resolution photoelectron spectroscopy (REMPI-PES) constitutes a powerful tool for obtaining detailed information on the spectroscopy and the dynamics of molecular excited states. The application of the method to relatively small molecules, in particular simple gas phase radicals, can be very enlightening. Such elusive species (e.g., OH, NH, SH, ClO, CIS) often play a predominant role as short-lived intermediates in atmospheric reactions under the influence of solar radiation and in combustion processes, and may occur as long-lived molecules in circumstellar space.

An important advantage of studying small molecules is that they are amenable to sophisticated quantum chemical calculations. In general the interplay between theory and REMPI-PES experiments is unusually strong and productive. Electronic structure calculations of excited and ionic states can be carried out in great detail, and often reliable predictions can be made about perturbations of electronic, vibrational and rotational states, and about configuration interaction. Since REMPI-PES is the method of choice for making chemically important effects of configuration interaction and various types of perturbations experimentally 'visible', some illustrative examples will be discussed.

As small radicals possess relatively large rotational constants, *rotationally resolved* photoelectron spectroscopy is often possible, both with and without ZEKE detection. By keeping track of all the angular momenta which play a role in the photoionization experiment much can be learned about the dynamics of the entire process. Again, a close interaction with quantum chemical theory allows the elucidation of various subtle effects such as those due to the anisotropy of the intramolecular potential, orbital mixing, and Cooper minima.

Recent research in our laboratory on the SH radical shows some unusual results. Strong asymmetries in the rotational branching ratios in REMPI-PES via the $[a\ ^1\Delta] \ 3d\pi\ ^2\Phi\ (v'=0)$ Rydberg state of SH have been observed. These asymmetries are a clear indication for large deviations from a simple classical picture in which gaining or losing angular momentum is equally probable. Moreover, work on the $[a\ ^1\Delta] \ 5p\pi\ ^2\Phi\ (v'=0)$ state, located above the lowest ionization energy, indicates that absorption of an additional photon is a more probable process than autoionization into the underlying continua, thus contradicting the common notion that for superexcited states the autoionization decay channel strongly dominates.

DOUBLE PHOTOIONIZATION PROCESSES STUDIED BY THRESHOLD-PHOTOELECTRONS COINCIDENCE

M.Hochlaf, R.I.Hall, H.Kjeldsen, F.Penent,
P.Lablanquie[§], M.Lavollée[§], J.H.D.Eland⁺ and S. Hsieh⁺

LDMA, Université P&M Curie, 4 Pl.Jussieu, 75252 Paris 05, France

[§]LURE, Université Paris Sud, 91405 Orsay, France

⁺Physical Chemistry Laboratory, Oxford OX1 3QZ, UK

The interest in studying valence double-photoionization has increased recently with the development of high brilliance synchrotron sources and improved coincidence techniques. These have finally allowed the direct observation of a process^{1,2} forbidden in first approximation (independant electrons model) for which cross-section vanishes at threshold. This underlines the importance of electron-electron correlations in this process but also the high sensitivity of new experiments. Our goals in this study are: i) direct spectroscopy of dication, ii) study of state to state dissociation processes ...

The experiment was performed using synchrotron radiation from the 800MeV Super ACO storage ring at LURE. The experimental method is based on Threshold PhotoElectrons COincidence technique (TPEsCO)¹: a small penetrating field collects threshold electrons (energy less than 20meV) with high efficiency (4π solid angle) and guides them into a single electron analyser. Electron pairs from double-photoionization are recognised by recording coincidences on one microchannel plate assembly (autocorrelation technique). To avoid parasitic signal due to energetic electrons (single ionization) two different methods were used:

- time of flight filtering of threshold electrons³
- use of hemispherical electrostatic analyser to select threshold electrons.

Results obtained with the two set-ups will be presented.

- Threshold double photoionization of rare gases: in Argon the $^3P_{2,1,0}$ Ar⁺⁺ states formation is strongly influenced by the excitation of highly excited Ar⁺* states decaying towards Ar⁺⁺ $^3P_{2,1,0}$. A large difference between the observed branching ratios towards Ar⁺⁺ $^3P_{j=2,1,0}$ and the statistical ratios was observed.
- With an improved energy resolution of 30meV the vibrational states of N₂⁺⁺ can be now clearly separated. This allows the identification of the three overlapping vibrational progressions $^1\Sigma_g^+$, $^3\Pi_u$ and $^1\Pi_u$ first observed by Dawber *et al*⁴.
- Direct observation of vibrational levels in triatomic dication at the CO₂⁺⁺ threshold...

Since the two electrons are detected on the same detector the other side of the experiment is available for ion detection allowing further studies of dications fragmentation.

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Fragmentation dynamics of core-excited molecules

F. Heiser, O. Geßner, K. Wieliczek, N. Saito*, and U. Becker

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin 33, Germany

*Electrotechnical Laboratory, 1-1-4, Umezono, Tsukuba-shi, Ibaraki 305 JAPAN

Since the discovery of strong angle dependences in the ionic fragmentation of core-excited gas-phase molecules this effect has been successfully utilized for studying the molecular symmetry of core-excited states. These studies determined the molecular anisotropy parameter β_m , a quantity which describes the dependency of the absorption strength on the molecular orientation with respect to the electric vector of the exciting synchrotron radiation photon beam. Whereas the interpretation of β_m for diatomic molecules is straight forward it is less unambiguous for triatomic molecules as, for example, CO₂. In most cases the experiments give average values for preferred orientations depending on the geometry of the molecule.

A new type of experiment is possible, if the corresponding outgoing electrons are registered additionally. The angular distribution of photoelectrons from molecules fixed in space can then be determined. This angular distribution is completely different from the angular distribution of randomly oriented targets because the additional quantization axis, now introduced by the target polarization, makes it possible to disentangle the various orbital angular momentum components of the emitted photoelectrons. First measurements of the angular distribution of photoelectrons from oriented molecules are described. The experiments employ angle-resolved photoelectron-photoion coincidences (ARPEP-ICO) in order to determine the position of the molecule in space at the moment of photoionization.

POLARIZATION OF MOLECULES BY NON-RESONANT LASER FIELDS

Bretislav Friedrich and Dudley Herschbach

Department of Chemistry, Harvard University, Cambridge, MA 02138, U.S.A.

The nonresonant interaction of intense laser radiation with molecular polarizability [1] can be used to create aligned pendular states. This method is applicable regardless of whether or not the molecule is polar or paramagnetic. Furthermore, the polarizability interaction seems likely to provide a means to trap molecules in a fashion similar to the far off resonance technique for atoms [2].

A linear molecule (polar or non-polar) irradiated by a plane wave $\varepsilon = \varepsilon_0 \cos(2\pi\nu t)$ of amplitude ε_0 and nonresonant frequency ν whose reciprocal is much smaller than the pulse duration is subject to a purely attractive mean potential, $-(\omega_{\perp} + \Delta\omega \cos^2 \theta)$, with θ the angle between the molecular axis and the vector ε . Here $\Delta\omega = \omega_{\parallel} - \omega_{\perp}$; the dimensionless parameters ω_{\parallel} and ω_{\perp} , proportional to components α_{\parallel} and α_{\perp} of the molecular *polarizability*, measure the potential energy of the induced dipole parallel and perpendicular to the molecular axis in terms of the rotational constant [3]. The corresponding Schrödinger eigenfunctions are readily obtained from tabulated oblate spheroidal wavefunctions [4]. These eigenstates are *directional hybrids* of the molecular field-free rotor states in which the axis of the molecule is aligned along the field. The isotropic part of the potential, ω_{\perp} , lowers all states uniformly, and the anisotropic part, $\Delta\omega$, responsible for the hybridization, introduces a double-well corresponding to the end-for-end symmetry. The hybrid states bound within these wells (*pendular states*) hence occur in pairs, split by tunneling through the barrier between the wells.

Spatial trapping by even a cw laser field appears feasible. For instance, high-finesse cavities can provide cw laser intensities of $I = 5 \times 10^{10} \text{ W/cm}^2$ within a small volume of about 10^{-9} cm^3 at the waist of a focussed infrared beam. For a fairly polarizable molecule, like CS_2 , the ground pendular state in such a "pocket of light" then corresponds to a trap depth of about 4 K. That is quite sufficient to enable use of collisional relaxation with a cold buffer gas (${}^3\text{He}$ at 0.25 K) to load the trap [5]. Lifetimes in the trap may be long (~hours), if limited by photon recoil heating, which is very feeble in the infrared.

Strong laser fields thus offer a promising means to both align and trap molecules and thereby to further enhance the resolution of stereodynamical experiments.

Spectra of pendular states produced by the polarizability interaction are distinctive and can be used for their detection. The selection rule for electric dipole transitions between pendular states is $\Delta\tilde{J} \equiv \tilde{J}' - \tilde{J}'' = \pm 1, \pm 3, \pm 5, \dots$. The field dependence of the frequency of a given transition can be used to evaluate the molecular-axis alignment of the states involved in the transition [1].

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The Interaction of Atoms and Molecules with Intense Laser Radiation

M H R Hutchinson

The Blackett Laboratory, Imperial College, London SW7 2BZ

Short pulse laser systems using the technique of chirped pulse amplification [1] are capable of producing powers in excess of 1TW, producing intensities in excess of 10^{17}W/cm^2 when focused. Under these extreme conditions, atoms and molecules behave in a highly nonlinear fashion to give rise to such phenomena as multiphoton and tunnelling ionisation [2], the production of short-wavelength coherent radiation by high harmonic radiation [3] and bond softening and dissociation of molecules [4,5].

At modest intensities ($<10^{13}\text{W/cm}^2$), the interaction with an atom or molecule may be described by a perturbative treatment, and gives rise to harmonic generation and above threshold ionisation (ATI). At higher intensities, an electron is driven by the optical field and produces ionisation by tunnelling or, through the resulting interaction of the oscillating packet with the atomic core, to the generation of very high order harmonics. Experiments will be described in which harmonics of order up to 119 have been produced [6], producing radiation of wavelengths down to $\sim 9\text{nm}$. The characteristics of this radiation will be discussed together with the extension of the technique to diatomic and organic molecules. The possibility of intensification of the radiation by amplification in X-ray amplifiers will be discussed.

Molecules have additional degrees of freedom due to vibration and rotation and phenomena such as above threshold dissociation (ATD) [4,5] may take place. Moreover, there is evidence that dissociation may be controlled by the coherent superposition of two phase-related frequencies of laser radiation. Results of recent experiments will be reported.

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SPECIES-SELECTIVE STUDIES OF INTERMOLECULAR
RESONANCES IN MOLECULAR CLUSTERS
BY NONLINEAR RAMAN SPECTROSCOPY

Peter M. Felker

Department of Chemistry
University of California
Los Angeles, California 90095-1569
U.S.A.

Recent advances in mass-selective, ionization-detected stimulated Raman spectroscopy (IDSRS) have allowed for the species-specific measurement of *intermolecular* transitions in molecular clusters across a wide spectral range with subwavenumber resolution. Such measurements hold out the promise of revealing much about intermolecular potential energy surfaces and collective molecular motions. Results from intermolecular IDSRS experiments on jet-cooled clusters such as benzene-(water)_n (n=1 to 5) and naphthalene_n (n=3 and 4) will be presented and discussed.

COMPETITIVE INTERNAL TRANSFERS IN METASTABLE DECAY OF CLUSTER IONS

G. Delgado-Barrio, M. Pilar de Lara, S. Miret-Artés, P. Villarreal

Instituto de Matemáticas y Física Fundamental, C.S.I.C.

Serrano 123, 28006 Madrid, SPAIN

E. Buonomo and F.A. Gianturco

Department of Chemistry, The University of Rome

Cittá Universitaria 00185 Rome, ITALY

Several studies of the unimolecular fragmentation dynamics of Ar_3^+ [1,2] and Ar_n^+ (with $6 \leq n \leq 27$) [3] complexes have indicated the role of overall rotations in leading to unexpectedly long lifetimes for these ionic clusters, according to experimental observations. In an earlier analysis only an effective one dimensional potential model was employed to describe such metastability effects in the evaporation process of the ionized argon clusters. Later, a two dimensional model which accounted for the stretching-bending motion of the Ar atom with respect to the Ar_2^+ dimer, which in turn was kept fixed at its equilibrium distance [2], provided the first attempt at examining the role played by internal energy transfer, in this case by rotational predissociation, in guiding the Ar_3^+ fragmentation. A new three-dimensional potential energy surface of the ground electronic state of the Ar_3^+ cluster has been computed within a density functional framework and employed in a dynamical study of the vibrational predissociation channel as a possible fragmentation pathway for the complex [4,5]. Both predissociation mechanisms have led to very short lifetimes. These lifetimes can be lengthened only when overall rotational states are included, confirming the physical picture of the earlier works [1,3].

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Time evolution in van der Waals reactive clusters

C. Jouvet

Laboratoire de Photophysique Moléculaire du CNRS

Bat 213, Université de Paris Sud

Optical excitation of van der Waals complexes or clusters give the opportunity to access to the intermediate state of reaction and to measure directly the reaction times in these pseudo binary reactions.

Two examples of such reactions will be presented.

The reaction of $Xe_n \dots Cl_2$ leading to $XeCl^*(C,D)$ have been studied through direct VUV excitation of the intermediate charge transfer state $Xe^+--Cl_2^-$.

Reaction occurring in the ground state, after the photodissociation of Cl_2 within the cluster has been investigated through femtosecond pump probe experiments. Three reactive processes occurring within 2ps are evidenced.

The ionic substitution reaction in Fluoro-Chloro-Benzene...(NH₃)_{1,2} pioneer by B. Brustch, has been revisited through REMPI and TPIEPCO (Threshold PhotoIon PhotoElectron Coincidence) method. One have evidenced two reaction paths :

-one occurring at high energy, the CL elimination, with a reaction time in the nanosecond domain

-at low energy, the HCl elimination is the only channel open, with a reaction time in the microsecond domain.

The reaction mechanism is deduced from the energetic and kinetic measurements.

Optical spectroscopy of ionized rare gas clusters

B.v.Issendorff

Universität Freiburg, H.Herderstr. 3, 79104 Freiburg, Germany*

Ionized rare gas clusters are relatively simple systems, which can serve as model systems for the study of a number of very different problems, like the influence of electronic correlation on the geometric structure of the cluster or the role of nonadiabatic transitions in the dissociation dynamics.

In contrast to many other clusters or molecules the ionized entities differ strongly from their neutral counterparts. Neutral rare gas clusters are van-der-Waals bound due to their closed valence shells, and their lowest excitations require energies of more than 10 eV. In ionized clusters, however, one electron is missing in an antibonding orbital, which leads to a much stronger bonding and a number of low lying excited states, which in turn opens the possibility to examine these species by optical spectroscopy.

One central problem the numerous studies of this system have been aiming at is the question on what entity the charge is located within the cluster. Soon after first observations of ionized rare gas clusters it was recognized that the positive charge inside the cluster will not stay on a single atom, but that due to the strong binding energy of ionized rare gas dimers it is energetically favourable if a charged dimer is formed within the cluster [1]. Theoretical studies indicate that a linear charged core out of three or four atoms, with the other atoms attached to by polarization forces, will be the most favourable structure [2,3].

Most of the experimental studies which have been done so far are photodissociation experiments, measuring photoabsorption cross sections [4,5] or, more recently, the kinetic energy release to the photofragments [6-8].

These experiments have been performed on nearly all of the rare gases for a broad range of cluster sizes, and have demonstrated for example that in all cases in the smaller clusters the charge is indeed localized on a linear trimer core structure.

More detailed information about the clusters and their fragmentation dynamics is yielded by measurements of the photofragment center-of-mass velocity and angular distributions, which have turned out to be especially valuable for this system. A number of results has been obtained in this way like the observation of linear isomers of the charged argon and xenon tetramers, the demonstration of the influence of spin-orbit coupling and of vibrational excitation on the fragmentation of the charged argon and xenon trimers [7], or the unexpected observation of metastable electronically excited He_4^+ [8].

These findings together with new theoretical results add to a relatively good overall understanding of the properties of the ionized rare gas clusters, but have also revealed new interesting details which wait for further examination.

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*present address: University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

Single-molecule Magnetic Resonance Spectroscopy

J. Schmidt

Huygens Laboratory, University of Leiden, The Netherlands

It has been demonstrated recently that it is possible to observe the magnetic resonance signal of a single molecular spin. This achievement represents the ultimate sensitivity in Electron Spin Resonance spectroscopy, where usually 10^{11} spins are needed to observe the EPR spectrum. In this presentation I will describe how a single molecule in a molecular crystal can be selected using a cw, narrow-band laser. Then I will demonstrate how the magnetic resonance transition in the metastable triplet state can be detected as a change in the intensity of the fluorescence. This experiment allows us to check whether the time-averaged signal of a single spin is equal to the result of an ensemble average i.e. whether the Ergodic Theorem applies. The conditions for the fulfilment of this theorem will be discussed.

Recently we have been able to perform single-spin experiments on molecules containing one ^{13}C atom in natural abundance. The presence of the single ^{13}C nuclear spin ($I = \frac{1}{2}$) is clearly visible via its effect on the lineshape of the zero-field transition. When applying a magnetic field the hyperfine splitting of the single spin resonance signal is clearly observed. This experiment opens the way to perform magnetic resonance experiments on a single nuclear spin.

Collective Optical Properties of Molecular Assemblies

Jasper Knoester

Theoretical Physics, Materials Science Center
University of Groningen, 9747 AG Groningen
The Netherlands

In this contribution, I will discuss the collective optical properties of assemblies of interacting molecules. Such nanostructures have attracted much attention over recent years, both for fundamental and for technological reasons. Examples are molecular J-aggregates, which are commonly believed to be quasi-one-dimensional, and Langmuir-Blodgett monolayers. The delocalization of the eigenstates (excitons) in these systems causes collective effects in the optical response. Well-known collective effects are: exciton superradiance, motional line-narrowing, and size-enhancement of optical hyperpolarizabilities.

In this talk, I plan to focus on the nonlinear optical properties of one-dimensional J-aggregates. The standard and exactly solvable Frenkel exciton description for a chain of N coupled two-level molecules will be put forward and some of its consequences will be discussed. Particular attention will be paid to the existence of multi-exciton states and to effects of disorder on the phenomenon of giant (size-enhanced) nonlinearities. In addition, I will go beyond the standard model and discuss novel analytical results for chains of three-level molecules. Even though it is impossible to find all 3^N eigenstates for such a system, it turns out that all one- and two-photon active states can be found exactly. This enables one to calculate the linear and third-order nonlinear optical response. I will focus on the nonlinear absorption spectrum and discuss how individual (intramolecular) and collective (intermolecular) two-photon absorption effects interfere.¹ Depending on the system parameters, the third molecular level gives rise to zero, one, or two additional two-photon absorption peaks in the nonlinear absorption spectrum.

Recent experiments on J-aggregates of the dye pseudo-isocyanine will be discussed in the light of the theory presented.

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Towards an understanding of elementary photochemical reactions in condensed phase.

N. Schwentner

Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin

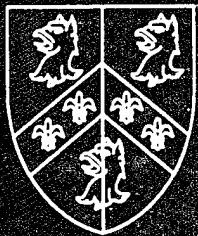
The dissociation of small molecules like HCl, H₂O, Cl₂ and F₂ in an inert and well ordered crystalline surrounding will be considered as an elementary photoreaction and the cage effect will be discussed. A combination of laser and synchrotron radiation allowed to study a large range of kinetic energies of the fragments. The observed dependence of the dissoziation efficiency on excess energy, temperature and structure of the rare gas matrix raised questions with regard to the duration of the cage exit, the energy dissipation rate and the range of the fragments. These problems were treated successfully by molecular dynamics simulations which incorporated nonadabatic transitions on advanced potential surfaces. The detailed predictions are tested at present experimentally on a femtosecond time scale by resonance Raman scattering and by ultrashort time pump-probe spectroscopy. An extension to quantum control of the fragment dynamics will be discussed. New results on long range migration of hot fragments like F atoms from F₂ dissociation derived from transport through sandwich type samples will be presented.

EIGHTH EUROPEAN WORKSHOP

**POSTER
PRESENTATIONS**



MOLECULAR SPECTROSCOPY PHOTON INDUCED DYNAMICS



**EIGHTH
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3RD - 7TH SEPTEMBER 1995

EIGHTH EUROPEAN WORKSHOP ON MOLECULAR SPECTROSCOPY

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3rd - 7th September 1995

at

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Address for all correspondence:

8th European Workshop,
Physical and Theoretical Chemistry Laboratory,
South Parks Road,
OXFORD OX1 3QZ
U.K.

FAX: (44)-(0)-1865-275410
e-mail: jpsimons@vax.ox.ac.uk
or eland@vax.ox.ac.uk

ORGANISATION

Arrival and registration

The Workshop registration desk will be open at Trinity College on Sunday September 3rd from 6pm to 8pm, and in the foyer of the Physical and Theoretical Chemistry Laboratory (PTCL) on Monday morning, September 4th, from 9.30 am to 11 am when the meeting opens. Delegates arriving on Monday morning can go first to Trinity College to be given their rooms, then go on to the laboratory.

Accommodation and meals

All delegates, except those who have made special arrangements will be lodged in Trinity College. All meals, including the conference banquet on Thursday evening, will be taken in the College, except for lunch on Wednesday 6th at the Rutherford Appleton Laboratory. Coffee and tea will be available at the breaks in the lecture sessions. Some free drinks will accompany the poster sessions, and a bar will be available.

Travel arrangements

The conference site is easily reached by air (Heathrow or Gatwick airports), by train or by coach. There is a frequent bus service during weekdays covering the College, the Laboratory and the coach station, but all these are also within walking distance of each other.

Arrival by air. The most convenient airport is Heathrow, where there is a frequent and fast (ca. one hour) coach service (X70) to Oxford from the central bus station and from Terminal 4. The same coach also serves Gatwick at less frequent intervals. Get off in Oxford at the terminus (Gloucester Green); Trinity College is a short walk away due East along George Street and straight on at the traffic lights into Broad Street.

Arrival via London. Eurostar trains arrive in London at Waterloo station. To travel on by train, take the Underground Bakerloo line (brown on network maps) direct to Paddington station, where there are trains to Oxford. Alternatively, to travel on by coach go to the coach station at Victoria (Underground Bakerloo or Northern line to Embankment, change to Circle or District line (eastbound) to Victoria). Fast coaches (Citylink X90) leave Victoria about every twenty minutes, and arrive in Oxford at Gloucester Green, like the airport coaches (above).

Arrival in Oxford by rail. The railway station is just a bit too far from Trinity College to walk there with luggage. On Sunday take a taxi outside the station. On weekdays an electric bus (City Circle) leaves the station every ten minutes and passes Trinity College.

Social programme

The afternoon of Tuesday 5th has been set aside for individual exploration of the city or participation in organised activities.

These are:

1. Walking tours of the Colleges with amateur (mainly student) guides. Great historical erudition cannot be guaranteed, but intimate knowledge of present University life is likely.
2. Punting on the river Cherwell. This is a very pleasant and relaxing activity for a fine day. Participants will be offered the chance to take their turn with the punt pole. Informal dress is advised.

If you would like to take part in one of these activities, please register your interest with the organisers **on arrival** so that provision can be made for the numbers required.

Posters

Two poster sessions are scheduled, but there will be enough room for all the posters to be on display all the time. Each poster's owners will be asked to defend it during one session, to be notified at arrival time, but will be free to browse other posters during the other session.

The size of the poster boards is 1.2x1.2 m.

Visual aids

Two overhead transparency projectors and a standard 2x2" slide projector will be available in the lecture theatre. Please let the organisers know in good time if you want any other facilities such as video or cine projection.

Lectures

All lectures are allocated 45 minutes **including discussion**.

Please plan your oral presentation to last no longer than 35 minutes. The programme is very tight, and session chairman are expected to enforce strict time discipline.

Programme

Sunday

6-8 pm Registration at Trinity College. A buffet supper will be available from 6.30 pm.

Monday

7.45 am ***** breakfast in Trinity *****

9.30-11 Registration and coffee in the PTCL

11 am Opening ceremony-- Prof. J.P. Simons

Session 1: Photon-induced dynamics in the gas phase

Chairman: Prof. J.P. Simons

11.15 Prof. C. Wittig, "The photophysics and photochemistry of NO_2 "

12.00 Dr. J. Vigué, "Spectroscopy and photodissociation of oriented molecules"

1 pm ***** LUNCH *****

Session 2: More photon-induced dynamics

Chairman: Dr. G. Hancock

2.30 Dr. H. Bitto, "Intersystem crossing studied by high resolution quantum beat spectroscopy"

3.15 Prof. R.J. Gordon, "Coherent control of unimolecular reactions"

4.00 ***** tea *****

4.30 Dr. D.E. Manolopoulos, "Quantum and semiclassical theories for photodissociation"

5.15 Prof. A. Kupperman, "A strong geometric phase resonance in the
 $H + D_2 = HD + D$ reaction"

6.00 Prof. M.N.R. Ashfold, "High resolution photofragment translational spectroscopy"

7.00 ***** DINNER *****

8.30 First Poster session: Group A.

Tuesday

7.45 am ***** Breakfast *****

Session 3: Spectroscopy and photon-induced dynamics at interfaces

Chairman: Dr. H. Lefevre-Brion

9.00 Prof. P. Guyot-Sionnest, "Vibrational surface dynamics"

9.45 Dr. C.D. Bain, "Structure and phase transitions of monolayers of n-alcohols on water"

10.30 ***** Coffee ***

23

Session 4: Photon-induced processes in extraterrestrial environments

Chairman: Prof. J. Rostas

11.00 Prof. J.P. Maier, "Spectroscopy of carbon chains of relevance to astrophysics"

11.45 Dr. J. Tennyson, "Infrared observations of the impact
of comet Shoemaker-Levy-9 with Jupiter"

1 pm ***** LUNCH *****

2.30 College tours, punting etc.

7.00 ***** DINNER *****

8.30 Second Poster session-Group B

Wednesday

7.45 am ***** Breakfast *****

8.45 Coaches depart for RAL

Session 5: Photon-induced processes and spectroscopy in the VUV

Chairman: Dr. J.H.D. Eland

9.15 Prof. C. deLange, "Laser photoelectron spectroscopy: chemistry with a light touch"

10.00 Dr. F. Penent, "Double photoionization processes studied by
threshold photoelectrons coincidence"

10.45 ***** Coffee *****

11.00 Dr. F. Heiser, "Fragmentation dynamics of core-excited molecules"

Session 6: Atoms and molecules in intense fields

Chairman: Dr. T.P. Softley

11.45 Dr. B. Friedrich, "Polarisation of molecules by non-resonant laser fields"

12.30 Prof. M.H.R. Hutchinson, "The interaction of atoms and molecules
with intense laser radiation"

1.15 pm ***** LUNCH *****

Wednesday (cont.)

- 2.15 *Introduction to the Central Laser Facility - Prof. Mike Key*
2.45 Tour of the central laser facility

4.00 ***** tea *****
4.30 Coaches leave RAL for Oxford

7.00 ***** DINNER *****

8.30 Bar open for informal discussions

Thursday

- 7.45 am ***** Breakfast *****

Session 7: Spectroscopy and dynamics in van der Waals complexes and clusters

Chairman: Dr. M. Gonzalez

- 9.00 Dr. P.M. Felker, "Species-selective studies of intramolecular resonances
 in molecular clusters by non-linear Raman spectroscopy"
9.45 Dr. G. Delgado-Barrio, "Competitive internal transfers in metastable decay
 of cluster ions"
10.30 ***** coffee *****
11.00 Dr. C. Jouvet, "Time evolution in van der Waals reactive clusters"
11.45 Dr. B. von Issendorff, "Optical spectroscopy of ionized rare gas clusters"
1 pm ***** LUNCH *****

Session 8: Photon-induced processes and molecular spectroscopy in condensed phases

Chairman: Prof. A. Beswick

- 2.30 Prof. J. Schmidt, "Single molecule magnetic resonance spectroscopy"
3.15 Prof. J. Knoester, "Collective optical properties of molecular assemblies"
4.00 ***** tea *****
4.30 Dr. N. Schwentner, "Towards an understanding of elementary photochemical reactions
 in condensed phases"
5.15 Dr. D. Klug, "Relaxation dynamics in proteins studied by ultrafast spectroscopy"

6.00 Closing remarks - Prof. V. Aquilanti.

7.30 ***** CONFERENCE BANQUET *****

EIGHTH EUROPEAN WORKSHOP

**POSTER
SESSION A**

NON ADIABATIC PROCESSES IN COLLISIONS BETWEEN RUBIDIUM IONS AND SODIUM NEUTRAL ATOMS BY CROSSED MOLECULAR BEAMS

J. de Andrés, A. Aguilar, T. Romero, M. Albertí, M. Prieto, J.M. Lucas and J. Rubio

Dept. de Química Física, Universitat de Barcelona. Cl. Martí i Franquès 1, 08028 BARCELONA (SPAIN).

We are involved in the study of collision processes between metal atoms and alkali ions, using a crossed molecular beams apparatus. Thus, Na collisions with Na^+ , K^+ , and Cs^+ , have been studied in the energy range 0.5 - 5.0 keV, both electronic excitation and electron capture collisional processes have been studied by measuring the fluorescence due to the decay of the excited species formed [1]. In some cases, signal strength allowed their state-to-state resolution [2].

This contribution deals with results obtained for the $\text{Na}-\text{Rb}^+$ collisional system, in which the cross-section dependence on collision energy for excitation channels $\text{Na}(3^2\text{S}_{1/2}) + \text{Rb}^+(1^1\text{S}_0) \rightarrow \text{Na}(\text{*}) + \text{Rb}^+(1^1\text{S}_0)$ (where $(*) = 3^2\text{P}_{1/2}, 3^2\text{P}_{3/2}, 7^2\text{S}_{1/2,3/2}, 6^2\text{D}_{5/2,3/2}, 5^2\text{D}_{5/2,3/2}, 4^2\text{D}_{5/2,3/2}$) and electron capture ones $\text{Rb}^+(1^1\text{S}_0) + \text{Na}(3^2\text{S}_{1/2}) \rightarrow \text{Rb}(\$) + \text{Na}^+(1^1\text{S}_0)$ (where $(\$) = 5^2\text{P}_{1/2}, 5^2\text{P}_{3/2}, 6^2\text{P}_{1/2,3/2}$), was determined in the 0.5-5.0 keV energy range.

E _{Lab} (eV)	Polarization (%)
1000	+15
1200	+13
1300	+6
1400	+7
1500	-9
1600	-2
1700	+2
1800	+6
1900	+1
2000	+16
2200	+11
2400	+11
2600	+7
3000	+5
3200	-1
3600	+4
4000	-6
4400	+1

Table 1. Polarization degree for the collisional electron-capture $\text{Rb}(5^2\text{P}_{1/2,3/2})$

Measurements of the polarization degree of $J=3/2$ component for the collisional excitation to $\text{Na}(3^2\text{P}_{1/2,3/2})$ and electron-capture $\text{Rb}(5^2\text{P}_{1/2,3/2})$, and their dependence on collision energy have been also made (see Table 1). From these the different m_J cross-sections can be determined.

In order to understand the system's dynamic behaviour, potential energy curves for these collisions have been calculated by using core polarization potentials [3]. In this approach the high reliability of ab initio calculations is combined with core polarization classical concept in order to obtain an efficient treatment of core-valence correlation for this pseudo one-electron system.

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ACKNOWLEDGEMENTS

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Effect of the vibrational excitation on the $\text{Cl} + \text{HD} \rightarrow \text{HCl}(\text{DCl}) + \text{D(H)}$ reaction

F. J. Aoiz and L. Bañares

Departamento de Química Física. Facultad de Química.
Universidad Complutense. 28040 Madrid, Spain

The $\text{Cl} + \text{HD}(v = 0, 1) \rightarrow \text{HCl}(\text{DCl}) + \text{D(H)}$ has been studied by means of quasiclassical trajectories on a new potential energy surface (PES) [1] at several collision energies. Whereas the scattering coming from $\text{HD}(v = 0)$ is found to be predominantly backward for both reactive channels, when the reaction is carried out with $\text{HD}(v = 1)$, the differential cross section (DCS) for HCl peaks strongly at 0 degrees. Moreover, it is found that this forward peak is highly specific, mainly coming from HCl formed in $v' = 1$ and relatively low j' values ($j' = 3 - 7$). The DCS for DCl production remains essentially backward with some small component into the forward direction. Similar results are obtained when the calculations are carried out on other similar PESs [2]. The rotational excitation of the HD has, contrary to the vibration, relatively little effect on the reaction with both ground and vibrationally excited HD .

Recent experiments on $\text{Cl} + \text{CH}_4$ show a similar behaviour [3,4], that is, the reaction with methane in the ground state produces backward scattered HCl , whilst the reaction with vibrationally excited CH_4 in $\nu_3 = 1$ gives rise to a forward peaked DCS for HCl scattering.

This propensity for forward scattering for $v = 1$ is explained in terms of the role of the impact parameter and the orientation of the reagents on a strongly collinear PES.

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Case Studies on Energy Transfer by Electronically Nonadiabatic Transitions*

V.Aquilanti, R.Candori, D.Cappelletti, and F.Pirani

Dipartimento di Chimica dell'Università, 06123 Perugia, Italy

The detailed mechanism which governs the redistribution of energy stored in a molecule when it encounters other species relies on the modalities of electronic nonadiabatic transitions.

In this presentation, recent experimental and theoretical progress is reported both on the proper representation of potential energy surfaces involved in nonadiabatic processes and on the formulation of the dynamics for the transitions. A few specific examples are discussed.

Although some features of potential energy surfaces relevant for inelastic and reactive molecular encounters can be obtained by quantum chemical calculations, the basic ingredients for their mapping are empirical, and rely on results from spectroscopic and molecular beam scattering techniques. Semiempirical correlation rules [1] allow characterization of features to the level of accuracy which is needed for the dynamics.

In turn, the dynamics requires development of formulas for transition probabilities which go beyond classic formulas, such as the Landau-Zener, to include tunneling and interference effects [2].

A further important aspect is the need of separating time scales for electronic transitions and redistribution of vibrational modes.

Examples from our work include the selective electronic energy transfer from a rare gas to nitrogen [3], the role of the vibronic manifold in an ion molecule reaction [4], and propensitivities for vibrational excitation in positive ion-negative ion recombination [5].

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VACUUM-UV FLUORESCENCE EXCITATION SPECTROSCOPY OF BCl_3 & BBr_3 :

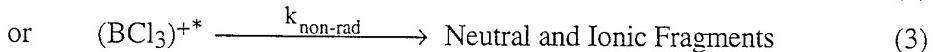
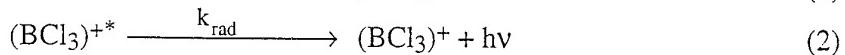
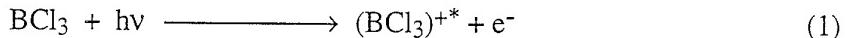
ELECTRONIC SPECTROSCOPY OF BCl_2 , BCl_2^+ , BCl_3^+ , BBr_2 , BBr_2^+ & BBr_3^+

H. Biehl, K. J. Boyle, D. M. Smith, R. P. Tuckett and K. R. Yoxall
 (School of Chemistry, University of Birmingham, Birmingham B15 2TT)

The growing importance of laser chemical vapour deposition techniques has meant that a critical re-examination of the photochemistry of several molecules used in such processes is important. BCl_3 is technologically important, as it is used in the plasma etching of silicon integrated circuits. A knowledge of its excitation, ionisation and fragmentation mechanisms is important to understand the physics of the plasma processes occurring under extreme discharge conditions. In such discharges molecular ions are created in an ill-defined way by high-energy (up to 30 eV) electrons. In this research project we are using the more controllable methods of *photon excitation* and *photoionisation* to study spectroscopy and fragmentation pathways. Three vacuum-UV photon excitation sources are used:

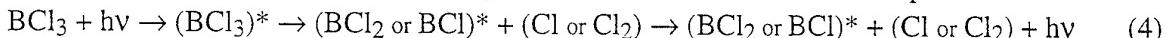
- Lyman- α (121.6 nm or 10.2 eV) radiation from a hydrogen discharge lamp with *dispersion* of the induced fluorescence from excited fragments through a (secondary) monochromator.
- Tunable radiation from the UK synchrotron source at Daresbury (50 - 140 nm or 8 - 25 eV) with *undispersed* fluorescence detection from fragments of the sample gas.
- Tunable radiation from the BESSY 1 German synchrotron source in Berlin (50 - 140 nm or 8 - 25 eV), with *dispersion* of the fluorescence through a (secondary) monochromator.

In general, excited ionic states of a polyatomic molecule such as BCl_3 created by photoionisation can decay radiatively by fluorescence or non-radiatively by a dissociative mechanism



where k is a decay rate. The fragment ions may also fluoresce if they are produced in excited electronic states. Fluorescence is a relatively rare phenomenon in polyatomic ions, where, because of the high density of states non-radiative processes occur much more rapidly than radiative decay, *i.e.* $k_{\text{non-rad}} \gg k_{\text{rad}}$. However, radiative decay from excited states of a range of polyatomic ions with T_d (e.g. CF_4^+), D_{3h} (BCl_3^+) and C_{3v} (CF_3Cl^+) symmetry has now been observed [1]. This observation is unexpected because these states lie up to 10 eV above many dissociation channels. Whilst such behaviour would not be surprising in diatomic ions, for larger, 4-5 atom polyatomics non-radiative processes would be expected to dominate the decay dynamics. The presence of such metastable ionic states with photon emission as their dominant decay pathway is one manifestation of non-statistical behaviour in these ions. Radiative decay from excited electronic states of polyatomic cations is measured at Daresbury. Thresholds for fluorescence are determined, and the fluorescence range is found with optical filters. Using the synchrotron source in its single-bunch mode the lifetime of the emitting state can be determined. Similar experiments are performed in Berlin, but with dispersion of the induced fluorescence through a small secondary monochromator; low-resolution electronic spectra of the emitting species are obtained this way [2]. The Birmingham experiment performs similarly except for using a fixed energy excitation source.

At photon energies below the first ionisation potential we have observed different, *neutral* dissociative processes leading to fluorescence. Rydberg states of the parent neutral molecule are photo-excited and dissociate with a substantial branching ratio into excited, fluorescing states of a fragment. The Rydberg states are observed as *resonant* peaks in the fluorescence excitation spectrum :



Information regarding the Rydberg states of the parent molecules and about the electronic spectroscopy of the neutral fragments is obtained. Emission spectra of BCl_2 and BCl have been observed. At higher photon energies we have observed emissions of both BCl_3^+ and BCl_2^+ [2]. Similar results are obtained for vacuum-UV photoexcitation of BBr_3 [3]. This is the first observation of a high-resolution spectrum in BCl_2^+ and BBr_2 .

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3. H. Biehl, D. M. Smith, R. P. Tuckett, K. R. Yoxall, H. Baumgartel, H-W. Jochims and U. Rockland, Mol. Phys., to be submitted

**THRESHOLD PHOTOELECTRON AND FLUORESCENCE COINCIDENCE
SPECTROSCOPY TO STUDY THE UNIMOLECULAR DECAY DYNAMICS OF
VALENCE ELECTRONIC STATES OF CF_4^+ , SiF_4^+ , SiCl_4^+ & GeCl_4^+**

K. J. Boyle, D. M. Smith, R. P. Tuckett, K. R. Yoxall, P. A. Hatherly and K. Codling
(School of Chemistry, University of Birmingham, Birmingham B15 2TT
and Department of Physics, University of Reading, Whiteknights, Reading RG6 2AF)

We are investigating the spectroscopy and decay dynamics of medium-sized (4 – 7 atoms) polyatomic ions in the gas phase [1]. For such ions, statistical factors might be expected to determine fragmentation channels; we are interested in the conditions under which *statistical* and *dynamical* factors dominate. Tuneable vacuum–UV radiation from the UK Synchrotron Radiation Source at Daresbury is used to photoionise molecules. Two monochromators are used to cover the 8 – 30 eV energy range: a 1 m Seya and a 5 m normal-incidence MacPherson, with ultimate resolutions of 0.05 and 0.01 nm respectively, often resulting in vibrational state selectivity. To define the vibronic state of the ion, we use a *threshold electron analyser*. Our analyser operates in the continuous mode, and takes advantage of chromatic aberrations in electron lenses [2]. It has very high resolution (~ 4 meV half-width) and high collection efficiency (*ca.* 30 % for zero-energy electrons). It is ideal for use in electron–ion coincidence experiments to study photofragmentation of state-selected molecular ions. In one apparatus we are able to perform three types of experiment on singly-charged ions. Coincidences may be detected between any two of threshold photoelectrons, ions (detected by TOF MS) and fluorescence photons. The three experiments are :

- (a) **Threshold PhotoElectron–PhotoIon Coincidences (TPEPICO)** allow the fragmentation channels of excited states of ions to be determined (usually to vibrational resolution). The channels that are observed and the *kinetic energy* released into these channels is an important guide to statistical or dynamical behaviour. This experiment is usually performed in the 'energy-scanning' mode. This allows thresholds for fragment ion production to be measured with an accuracy usually only obtained by photoionisation mass spectrometry.
- (b) **PhotoIon–Fluorescence Coincidences (PIFCO)** spectroscopy can determine whether an excited state of a molecular ion decays radiatively by photon emission, and can measure fluorescence quantum yields, Φ_F , and lifetimes, τ . However, the values of Φ_F and τ are averaged over the Franck–Condon populations of the vibrational levels of the fluorescing state. The technique can also give information on the fate of the lower electronic state to which fluorescence occurs, *e.g.* whether the state is bound or repulsive.
- (c) **Threshold PhotoElectron–Fluorescence Coincidences (TPEFCO)** also measure Φ_F and τ , but now the resolution is determined by that of the vacuum–UV ionising radiation and of the threshold electron analyser, usually affording vibrational resolution. This experiment is therefore superior to, but more demanding than the PIFCO experiment.

Using these three techniques, we have made an extensive study of the fragmentation of the valence states of CF_4^+ , SiF_4^+ , SiCl_4^+ and GeCl_4^+ [3]. Excited states of these ions decay both by radiative and non-radiative processes. Radiative decay from high-lying valence states of polyatomic ions is one manifestation of non-statistical behaviour, because non-radiative processes (especially internal conversion) should all occur much more rapidly due to the high density of states. By measuring the decay dynamics of these states at vibrational resolution, we learn about *intramolecular vibrational redistribution* within an isolated electronic state of the parent ion. An extensive study has been made of the C $^2\text{T}_2$ state of CF_4^+ over the Franck–Condon region of 21.4 – 23.6 eV. This state decays radiatively to repulsive lower electronic states which fragment to CF_3^+ and non-radiatively by direct dissociation or predissociation to CF_2^+ . Different vibrational levels of the CF_4^+ C state show varying branching ratios into these two decay channels. By measuring the lifetime of the vibrational levels by the TPEFCO technique, absolute values of radiative and non-radiative decay rates are obtained. The kinetic energy released into the fragment ions CF_2^+ and CF_3^+ confirms this interpretation.

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The use of the *sinc* interpolation in spectroscopy

by

J. Delwiche (1), L.F.A. Ferreira (2), K. Ibrahim (1,3),
D. Germain (1), P. Déry and D. Roy (4)

- (1) Université de Liège, Institut de Chimie, Bât. B6c, Sart Tilman par B-4000 Liège 1, Belgium.
- (2) Universidade de Lisboa, Ed. C2, Campo Grande, P-1700 Lisboa, Portugal.
- (3) Present address: CAS, Institute of High Energy Physics
SRL, Beijing, People's Republic of China.
- (4) Université Laval, Dépt. de Physique, Québec, QC G1K 7P4, Canada.

In spectroscopy measurements, several parameters have to be considered but in most cases their optimization are contradictory. For example, a good energy resolution is generally achieved by measuring the data points at small increments, but this means the inconvenience of longer acquisition times. Using the method of interpolation by the *sinc* function presents the advantage that the interpolated points have practically the same precision as the experimental points. This allows the measure of less experimental points without loss of resolution and not introducing additional noise. A computer application has been developed and applied to absorption, photoelectron and electron energy loss spectra.

Doppler-free spectroscopy and reaction imaging of doubly charged ion fragmentation

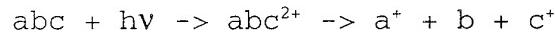
J.H.D. Eland and S. Hsieh,
Physical and Theoretical Chemistry Laboratory,
South Parks Road, Oxford, OX1 3QZ, U.K.

By combining a newly-developed position-sensitive detector for close-spaced ion pairs [1] with the PEPIPICO method we obtain full angle and energy information on each of the ions formed in dissociations of doubly charged parents. For two-body reactions,



the effect of parent molecule thermal velocity on measured momentum releases can be eliminated, giving Doppler-free kinetic energy release distributions. The full spatial distribution of fragments in LAB space (eg relative to the light polarisation direction) is also obtained, and will show any correlation between direction and energy release.

For three-body reactions,



we get the spectrum of total energy releases, including the neutral fragment energy. For each total energy release we have both LAB and CM spatial distributions. The mechanisms of fragmentation at each total energy can be seen in Newton diagrams giving the initial CM orientations of all three particle momentum vectors. Early results indicate that the mechanisms are more complex than hitherto supposed: the recent charge-exchange coulomb explosion model for fast decays [2] is being thoroughly tested.

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DYNAMICS OF THE O(¹D) + N₂O → NO + NO REACTION

Antonio Aguilar, Miguel González, Isidore Last, Ramón Sayós, Pedro A. Enríquez^a, Pilar Puyuelo^a
and Javier Guallar^b

Departament de Química Física, Universitat de Barcelona.
Martí i Franquès, 1. 08028 Barcelona, Spain

^a Departamento de Química, Universidad de La Rioja
Obispo Bustamante, 3. 26001 Logroño, Spain

^b Unidad Predepartamental de Física, Universidad de La Rioja
Luis de Ulloa, s/n. 26004 Logroño, Spain

ABSTRACT

The O(¹D) + N₂O → NO + NO reaction has been investigated experimentally by several groups [1-8]. The most recent studies examine the reaction using velocity aligned, superthermal O(¹D) atoms obtained via N₂O photodissociation at 193 nm [5-8] or photolysing the N₂O dimer to generate the reactant pair O(¹D)-N₂O [4]. From the theoretical point of view an ab initio calculation using the 6-31G basis [4] and a classical trajectory study employing a LEPS surface and modelling the NO of the N₂O molecule as a pseudoatom [9] have been reported.

As a part of an experimental and theoretical research project addressed to the systematic study of the stereodynamics of elementary reactions, we have carried out ab initio calculations of the planar N₂O₂ supermolecule in the ¹A' state using the 6-311G basis, and including electronic correlation mainly via the MP2 method. The reaction has a non-collinear minimum energy path (MEP) with a symmetrical trans-(O-N-N-O) minimum ($R_{ON}=1.211 \text{ \AA}$, $R_{NN}=1.279 \text{ \AA}$, ONN angle=138.3 degs.) 4.158 eV below reactants that has a barrier of 0.578 eV to products. The other possible reaction channel (N₂ + O₂(¹A_g)), that presents a comparable yield but has not been experimentally observed, exhibits a strongly non-collinear MEP with a O-O-N-N minimum with the original N₂O fragment still collinear ($R_{OO}=1.515 \text{ \AA}$, $R_{ON}=1.219 \text{ \AA}$, $R_{NN}=1.139 \text{ \AA}$, O-(ONN) angle=103.4 degs.) placed 1.236 eV below reactants and with a barrier of about 0.15 eV to products. From these data and additional ab initio points we have derived an analytical expression for the PES that describes the NO + NO reaction channel. At present we are performing classical trajectory calculations to check the validity of the fitted PES taking into account in the simulation the conditions of the experiments performed with O(¹D) atoms generated via photodissociation of N₂O. On the other hand, we are in the final step of verifying the correctness of a pump-probe (LIF) laser set up formed by a excimer photolysis laser and an electronically delayed excimer pumped dye laser. This system will be calibrated using this reaction and we hope to initiate new experiments on it in the close future. A detailed description and analysis of the most relevant results obtained will be presented in Oxford at the Eighth European Workshop of Molecular Spectroscopy and Photoinduced Dynamics (3-7 September 1995).

This work has been supported by the "Dirección General de Investigación Científica y Técnica" of the Spanish Ministry of Science and Education (DGICYT, Project PB92-0756). We would also like to thank Prof. Pedro J. Campos for his continuous support and encouragement, and to Dr. Irene Baños and Mr. Luis Zorzano for their help.

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**COMPUTATIONAL STUDY OF VECTOR CORRELATIONS IN
ELEMENTARY CHEMICAL REACTIONS.**

I. THE HYDROGEN ATOM TRANSFER PROCESSES



Miguel González^a, Rafael Francia^b, José Daniel Sierra^c and Ramón Sayós^a

^a Departament de Química Física, Universitat de Barcelona.
Martí i Franquès, 1. 08028 Barcelona, Spain

^b Departamento de Química, Universidad de La Rioja
Obispo Bustamante, 3. 26001 Logroño, Spain

^c Unidad Predepartamental de Física, Universidad de La Rioja
Luis de Ulloa, s/n. 26004 Logroño, Spain

ABSTRACT

Most of the experimental and theoretical efforts devoted to understand the dynamics of elementary gas phase reactions had focused on scalar properties. Although more difficult to deal with, mainly from the experimental point of view, vector properties should also be examined as they are key indicators of the anisotropy of molecular interactions. Hence, a complete understanding of reaction dynamics is only possible after accounting for both scalar and vector properties [1-3].

As a part of an experimental and theoretical research project addressed to the systematic study of the stereodynamics of elementary reactions, we have carried out a quasiclassical trajectory study of the kk' , $k'j'$, $l'j'$ and $kk'j'$ angular vector correlations in the ion-molecule systems $X^+ + H_2 \rightarrow XH^+ + H$ ($X^+ = C^+, N^+, O^+$). These processes may be considered as models for triatomic reactions with potential energy surfaces (PESs) that exhibit a well along the minimum energy path and **H-L-L** kinematics. We have examined the influence on the angular correlations of reagents translational, vibrational and rotational energies, and the effect of considering initial parallel or perpendicular alignments of the rotational angular momentum of H_2 and the reactants relative velocity vectors. The PESs employed are the same used in previous studies (C^+ [4], N^+ [5], O^+ [6]) on these systems largely centered on scalar properties. A detailed description and analysis of the most relevant results obtained will be presented in Oxford at the Eighth European Workshop of Molecular Spectroscopy and Photoinduced Dynamics (3-7 September 1995).

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Surface photochemistry with ultra-short laser pulses and the effect of morphology on the photoactivity of metal surfaces.

Malcolm Kadodwala, Hans G. Jenniskens and Aart W. Kleyn.

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam.
The Netherlands.

The influence of ultra-short (16ps) laser pulses on surface photochemistry of 1ML of methanol adsorbed on Ag(111) has been investigated. During laser irradiation the methanol molecule was found to desorb intact from the surface through a non-thermal process, no dissociation of the molecule occurred. Desorbing molecules had a translational temperature of 360 ± 30 K, which is hotter than the laser induced surface temperature. The cross-section for photodesorption was 1×10^{-19} cm² and was independent of incident laser power. When the experiments were repeated with nanosecond laser pulses methanol behaved in a similar way. However, the cross-section for photodesorption was an order of magnitude smaller (6×10^{-21} cm²). These experiments clearly indicate that photochemical processes can be enhanced using ultra-short laser pulses.

The photoactivity of 1ML of methanol adsorbed on a Ag(111) surface roughened by Ar+ bombardment and irradiated with 532nm pulses of 16ps duration has been investigated. This study was undertaken to determine whether the morphology of surfaces strongly influences their photochemical activity and complements work carried out on the well ordered single crystal surface.

As in experiments carried out on well ordered Ag(111), methanol was found to photodesorb from the surface with a cross-section of 1×10^{-19} cm² and with a translational temperature of 360 ± 30 K. However, a significant difference between the two surfaces was that a smaller amount of photodesorption occurred on the roughened surface. Only 20-30% of a monolayer of methanol could be photodesorbed from the roughened surface, whereas on the well ordered surface the complete monolayer could be desorbed. This indicates that even for weakly interacting physisorption systems there is a strong correlation between adsorption site and photoactivity.

A major difference between the well ordered and roughened surfaces was the observation of dissociation of methanol on the latter surface. The products of dissociation where adsorbed methoxy, water and a subsurface oxygen species. The presence of a sub-surface oxygen species is rather surprising. It indicates that an oxygen species which has enough energy to overcome the activation barrier to penetrate the surface is produced in the photolysis of methanol. The dissociation yield of methanol is highly non-linear with laser pulse energy, with almost complete dissociation of the monolayer at 50mJcm^{-2} , and no observable dissociation at 25mJcm^{-2} . When experiments were repeated with nanosecond laser pulses no dissociation of the methanol molecule was observed at high pulse energies. This clearly shows that excitation with ultra-short laser pulses open up new dissociation mechanisms for molecules at surfaces.

**FLASH PHOTOLYSIS-LASER-INDUCED FLUORESCENCE
MEASUREMENTS OF THE RATE CONSTANTS FOR REACTIONS OF
CAESIUM WITH CH₃Br, CF₃Br AND C₂H₅Br.**

Ernesto Martínez, José Albaladejo and Alberto Notario.

*Universidad de Castilla-La Mancha. Facultad de Química. Dpto. Química Física.
13071 Ciudad Real (SPAIN)*

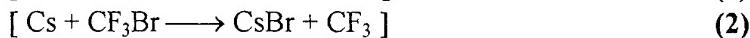
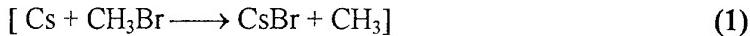
Abstract

Absolute rate data for reactions of the heavy alkali metal atoms in their electronic ground state constitute a developing component of the kinetic study of alkali atoms in general by spectroscopy methods.

The reaction of the alkali metal atoms with alkyl bromides is a class of reaction that has received much attention, for a variety of fundamental and applied reasons, in the last years.

A kinetic study is presented of the reaction between atomic caesium in its electronic ground state and various alkyl bromides in the gas phase by the technique of time-resolved laser-induced fluorescence spectroscopy and a study of diffusion of Cs in He at 780 K. Data for these reactions are compared with previous measurements made by time-resolved atomic resonance absorption spectroscopy.

The experiments were performed using a new constructed experimental system. Cs atoms were produced in an excess of reagent (CH₃Br, CF₃Br and C₂H₅Br) and He bath gas, by pulsed photolysis of CsBr vapour in equilibrium with its solid at elevated temperatures. The concentration of the metal atoms was monitored by LIF employing the shorter wavelength component of the strong spin-orbit resolved Rydberg doublet transition at $\lambda = 455.5$ nm (Cs(7p(²P_{3/2})) → Cs(6s(²S_{1/2}))), using a pulsed Nd-YAG-pumped dye laser and box-car integration of the fluorescence signal and transferred directly to a computer for kinetic analysis. The decay profiles were employed to characterise the absolute second-order rate constant K_R for the following reactions:



This yields (with standard errors)

Reaction (1): (K_R(780 K) = (2.43 ± 0.68) × 10⁻¹¹ cm³ mol⁻¹s⁻¹).

Reaction (2): (K_R(780 K) = (3.83 ± 0.97) × 10⁻¹¹ cm³ mol⁻¹s⁻¹).

Reaction (3): (K_R(780 K) = (4.18 ± 0.61) × 10⁻¹¹ cm³ mol⁻¹s⁻¹)

AN EXTENSION TO THE COUPLED RYDBERG-VALENCE MODEL FOR THE SINGLET UNGERADE ELECTRONIC STATES OF MOLECULAR NITROGEN

S. A. Edwards, W.-Ü. L. Tchang-Brillet and F. Rostas

DAMAP et URA 812 du CNRS, Observatoire de Paris-Meudon, F-92195 Meudon Cedex,
France.

We have extended the existing model [1] of the lowest lying singlet ungerade Rydberg and valence states of molecular nitrogen by the addition of rotationally excited energy levels and heterogeneous interactions between the electronic states.

The previous model of these electronic states was based on a least squares fit of the molecular parameters producing diabatic RKR potential curves and homogeneous interaction energies to the observed band origins of the vibrational bands of six electronic states (the $b'^1\Sigma_u^+$ and $b^1\Pi_u$ valence states and the $c'^1\Sigma_u^+$, $e'^1\Sigma_u^+$, $c^1\Pi_u$ and $o^1\Pi_u$ Rydberg states). In that work [1], since only the $J = 0$ levels were considered, heterogeneous interactions were neglected and the calculations were performed on two sets of three interacting excited electronic states.

Using the work of Stahel *et al.* as a basis we have continued the calculations for rotationally excited energy levels of the excited electronic states. This extension implies the inclusion of the known heterogeneous interaction between the p-complex c'-c together with the similar e'-e interaction. Thus we have included the $e^1\Pi_u$ electronic state in the model and have completely refitted the molecular parameters producing the diabatic potential energy curves together with the electronic interaction terms.

The least squares fit to nearly 2500 observed rovibronic term values has resulted in a much improved model for these electronic states, the standard deviation being 5.7 cm^{-1} (3.3 cm^{-1} for the $J = 0$ levels). The adiabatic wavefunctions resulting from our calculations and the decomposition into their diabatic components are being used to model the intensity distribution observed in the high resolution emission spectrum of N_2 and to improve the molecular transition moments with the aim of application to the study of planetary atmospheres.

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Product State Resolved Stereodynamics of the Reaction

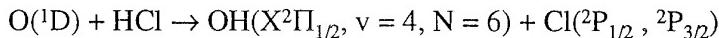


A. J. Alexander, M. Brouard, S. P. Rayner and J. P. Simons,

*Physical and Theoretical Chemistry Laboratory, South Parks Road,
Oxford, OX1 3QZ, United Kingdom.*

The reaction between $\text{O}(\text{^1D})$ atoms and HCl molecules has undergone extensive investigation in recent times, both theoretical and experimental [1,2,3,4]. Much of the interest in this system has concentrated upon the mechanisms behind the various channels which are thermochemically accessible. In particular, as with many other $\text{O}(\text{^1D})$ reactions, there is the question of whether the reaction proceeds *via* a long-lived collision complex (formed by 'insertion' of the oxygen atom into the HCl bond) or *via* a 'direct' mechanism.

The present study considered the following channel:



at a mean collision energy, $\langle E_T \rangle \sim 49 \text{ kJ mol}^{-1}$. The velocity-aligned oxygen atoms were produced by polarized photodissociation of N_2O at a wavelength of 193 nm, and the product OH molecules were probed in a state-selective manner via polarized Doppler-resolved laser spectroscopy.

Doppler-resolved profiles of individual rotational features in the (1,4) vibrational band of the $\text{A}^2\Sigma^+ - \text{X}^2\Pi_{1/2}$ laser induced fluorescence spectrum of the OH molecular product were measured and analysed to yield the laboratory speed distribution. A simulation technique [5] was then used to find the product state-resolved centre-of-mass differential cross-section for the scattered OH product. The experimental data could only be reproduced successfully if the integral and centre-of-mass differential cross-sections were allowed to display a dependence upon the reagents' collision energy.

In addition, the experimentally determined Doppler-resolved line profiles can be used to extract the angular momentum vector distributions of individual rovibrational states of the OH molecules. Using this method, a detailed picture of the reaction mechanism was constructed, and new information regarding the reactive scattering dynamics uncovered.

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High Resolution Electronic Spectroscopy of Jet-Cooled Molecular Conformers

P.A. Hepworth and J. McCombie

Department of Chemistry, The University, Nottingham, NG7 2RD, England

J.P. Simons

Physical and Theoretical Chemistry Laboratory, South Parks Road,

Oxford, OX1 3QZ, England

J.F. Pfanstiel, J.W. Ribblett and D.W. Pratt

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.

Rotationally resolved fluorescence excitation spectra in each of the $S_1 \leftarrow S_0$ origin bands associated with four conformers of methyl 3-hydroxy (and deutoxy) benzoate¹, and the two (and four) conformers of methyl (and ethyl) 3-amino benzoate¹ have been recorded². In all cases, analysis of the rotational structure has yielded rotational constants of both the ground and electronically excited states, their inertial defects and the *a/b* hybrid characters of the observed bands. It has been possible to assign the structure of each conformer band by comparing calculated inertial parameters with those obtained from experiment.

It has also been possible to determine the absolute alignment of the transition moment^{2,3} by subtracting the ‘inertial’ from the ‘electronic’ contribution to its rotations in the molecular frame. The ‘electronic’ contribution introduced by the methyl (or ethyl) ester substituent, is found to be constant, inducing a rotation of the transition moment through an angle $\sim 22^\circ$ towards the 2-position of the aromatic ring. The influence of substituents in rotating the polarization of the electronic transition, should be taken into account when molecular probes (such as tryptophan) are employed in the determination of biomolecular structures.

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On the Predissociation of the A²Π state of MgCl, MgBr and MgI

Fouad FETHI, Joëlle ROSTAS and Guy TAIEB

Laboratoire de Photophysique Moléculaire du CNRS
 Institut de Physico-Chimie Moléculaire de l'Université de Paris-Sud
 Bat. 213, Université de Paris-Sud, 91405 ORSAY Cedex, France

In a previous report¹, we presented an analysis of the laser excitation spectrum of the A²Π-X²Σ⁺ transition of MgCl, and experimental evidence for predissociation in the A²Π state. We recently recorded under medium resolution LIF spectra for Mg⁷⁹Br and Mg⁸¹Br in the 370-400 nm spectral region.

The MgBr radical is produced in a Broida oven through the reaction: Mg(¹S) + CHBr₃ ---> MgBr(X²Σ⁺) + CHBr₂. It is rotationally relaxed (T=350K) by a fast Helium flow. An excimer-pumped dye laser excites the X²Σ⁺ ground state to the A²Π excited state, the emission of which is collected through a monochromator used as a band filter.

The spectrum of MgBr consists of sequences of sharp heads degraded to the violet. Each sequence has two components separated by about 110 cm⁻¹. Both present a sudden cutoff of the vibrational structure, namely, at ν>2, and 1 respectively for the low energy and high energy component. A similar effect had been observed for the A-X transition of MgCl, where the vibrational structure disappears for ν>7. We suggested, then, that the vibrational structure cutoff as well as the anomalous behaviour of the A²Π state molecular constants might result from a strong interaction between the ...(3π)⁴(4π)¹ regular A²Π state and the repulsive inverted ...(3π)³,²Π state dissociating into the lowest states of the separate atoms Mg(¹S)+Cl(²P). This qualitative interpretation was put on a quantitative basis by a rigorous quantum mechanical treatment of the ²Π_Ω states of MgCl, incorporating spin-orbit and derivative coupling effects². It can be inferred that the same interpretation is valid in the case of MgBr, the avoided crossing between the two ²Π states being responsible for the predissociation and the anomalous r-dependence of the A²Π state parameters. The comparatively large spin-orbit coupling in MgBr tends to enhance some anomalies. However, since the predissociation sets in at very low ν_A, the experimental data set is much less extended than for MgCl, only "effective" molecular parameters can be determined from the available data. This set of parameters makes up a good basis for comparison with the results of *ab initio* calculations. An upper limit of 3.22 eV for the dissociation energy of the ground state of MgBr has been determined. The influence of the spin-orbit on the internal molecular dynamics can be tested within the MgX (X=Cl,Br,I) series.

¹ J. Rostas, N. Shafizadeh, G. Taïeb, B. Bourguignon and M.G. Prisant, 1990, *Chem.Phys.* **142**, 97.

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VIBRONIC STRUCTURE OF THE 3d-4s RYDBERG STATES OF ACETYLENE STUDIED BY REMPI

A. Campos, J.H. Fillion, N. Shafizadeh and D. Gauyacq

*Laboratoire de Photophysique Moléculaire, Bât. 213, Université de Paris-Sud
91405 ORSAY CEDEX (France)*

The interaction between a Rydberg electron and a vibronically excited core of a polyatomic molecule can be described with a model taking into account the degree of decoupling of the outer electron from the molecular core. When the core exhibits a strong vibronic coupling, as it is the case for the vibronically excited ground state of $C_2H_2^+, \tilde{X}^2\Pi_u$, one can expect a different structure of the Rydberg state, depending on the interaction between the Rydberg electron and the inner π electrons involved in the Renner-Teller interaction.

The Renner-Teller structure of the $\tilde{G}^1\Pi_u, 4s\sigma$ and $\tilde{H}^1\Pi_u, 3d\delta$ states has been first studied in absorption [1]. From the rotational analysis of several vibronic bands of the G-X and H-X transitions belonging to 4 isotopomers, and involving the v_4 and v_5 bending modes, the Renner-Teller structure of these Rydberg states of acetylene has been interpreted in terms of a Rydberg electron coupled to the core. Very recently, the same energy region has been studied by (3+1) REMPI of acetylene in a supersonic beam experiment [2]. Most of the 3 photon weak structure was assigned to Renner-Teller excited levels of the $\tilde{F}^1\Phi_u, 3d\delta$ Rydberg state, assuming a completely decoupled scheme for the Rydberg electron.

The region of the 3d-4s Rydberg complex of the acetylene molecule has been re-investigated by one-color (3+1) photon ionization at room temperature, with either linearly or circularly polarized light. In addition to the strong origin bands of the $\tilde{G}^1\Pi_u, 4s\sigma - \tilde{X}^1\Sigma_g^+$ and $\tilde{F}^1\Phi_u, 3d\delta - \tilde{X}^1\Sigma_g^+$ transitions, weaker bands have been assigned to vibronic bands associated with the trans-bent v_4 and cis-bent v_5 bending modes. The vibronic symmetry of the observed levels has been determined by comparing simulated rotational profiles with the observed spectra. Our analysis leads to a description of the Renner-Teller structure in the 4s and 3d states close to the coupled Rydberg electron description instead of a decoupled description as it was proposed in ref.[2].

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DYNAMICS OF THE HIGH LYING GERADE RYDBERG STATES OF ACETYLENE EXITED BY TWO-COLOR REMPI

J.H. Fillion, A. Campos, N. Shafizadeh and D. Gauyacq

*Laboratoire de Photophysique Moléculaire, Bât. 213, Université de Paris-Sud
91405 ORSAY CEDEX (France)*

Previous REMPI studies of the *gerade* Rydberg states of acetylene have shown that an efficient non radiative decay channel is opened above 9.4 eV ($n=4$), precluding any observation of the higher members of the np series with this technique [1]. Indeed, all Rydberg states are more or less predissociated and, consequently, must play an important role in the photofragmentation mechanism of acetylene in astrophysics. As shown by theoretical studies [2], the np Rydberg series show a good example of fast predissociation through a strong valence-Rydberg interaction in the 1A_g symmetry.

We have probed the high lying *gerade* np and nf Rydberg series by two-color ($3+1'$) photon excitation via the resonant $\tilde{G} \ ^1\Pi_u$, $4s\sigma$ ($v=0$) and $\tilde{F}' \ ^1\Phi_u$, $3d\delta$ ($v=0$) states. New Rydberg series have been observed for the first time by probing several rotational levels of the G and F' states. All these series have the same general appearance, from $n \approx 20$ up to $n \approx 45$. In the low energy range, ionization peaks are weak and broad. With increasing excitation energy, the ionization signal increases and the peak widths decrease, as it would be expected from a n-dependent predissociation mechanism. More surprisingly, REMPI spectra of Rydberg series, probed from the same rotational J value, but from different electronic intermediate states ($4s\sigma$ and $3d\delta$), look very similar. This observation most probably originates from a significant ℓ -mixing either in the upper states (p-f mixing) or in the intermediate state (s-d mixing). Ab initio calculations on this ℓ -mixing are in progress and should better characterize the symmetry of the intermediate states [3].

A more quantitative analysis using the multichannel quantum defect theory is needed in order to unambiguously assign the observed series and, eventually to deconvolute the spectra. This work is in progress.

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INTRAMOLECULAR AND PHOTODISSOCIATION DYNAMICS OF NO₃

L. Valachovic, C.W. Riehn, K. Mikhaylichenko, and C. Wittig

Department of Chemistry
University of Southern California
Los Angeles, California 90089-0482
U.S.A.

Intramolecular and dissociation dynamics of the nitrate radical have been investigated following laser excitation via the $^2E' \leftarrow ^2A_2'$ system (670-581.6 nm). NO₃ exhibits the Douglas effect and the LIF spectra indicate the presence of internal conversion processes. Spectroscopic features may be attributed to strong vibronic interactions, namely pseudo-Jahn-Teller coupling of \tilde{A}^2E'' and \tilde{X}^2A_2' vibrational levels to those of \tilde{B}^2E' . Investigation of the (0,0) band reveals that rotational temperature ($T_{\text{rot}} \approx 6$ K) and weaker interactions contribute, precluding a detailed interpretation of the nature of the mixed states. Effects of vibronic interaction are reflected in the dissociation dynamics. The channel for concerted reaction (NO + O₂) opens at $\lambda > 594.6 \pm 0.1$ nm [$^2E'$ (0,0,0,0) + 1700 cm⁻¹], and proceeds via the ground state surface. Dissociation is known to involve a tight transition state and a large reverse barrier. NO product yield spectra show clump-like features reminiscent of the excitation spectra. This channel has a narrow reaction window (~ 240 cm⁻¹: 594.6-585.5 nm). At the lower energies in this range, k(E) varies quite rapidly (3.5×10^5 to 3×10^7 s⁻¹ over ~ 80 cm⁻¹), while above what we judge to be the classical barrier, k(E) varies more slowly (1.5×10^9 to 3.5×10^9 s⁻¹ over ~ 200 cm⁻¹). The substantial k(E) variation at lower energies may be accounted for by a tunneling mechanism, as is possible for a reaction involving such a transition state. Product center-of-mass kinetic energy measurements indicate that O₂ is formed predominantly in the $^1\Delta$ state; however, at the lowest energies [i.e. smallest k(E)], O₂($^3\Sigma$) is also observed. When the NO₂ + O channel opens, the decomposition rate increases dramatically and reaction mainly proceeds via this channel; the NO product yield decreases rapidly.

**Time-of-Flight Measurements of the Kinetic Energies of the O₂(a¹Δ_g) Fragment
from the Photolysis of Ozone between 287 - 331nm.**

Stephen M. Ball, Gus Hancock, John C. Pinot de Moira,
Chester M. Sadowski and Fiona Winterbottom

Oxford Centre for Applied Kinetics,
Physical and Theoretical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford OX1 3QZ, U.K.

Abstract

The kinetic energies of the O₂(a¹Δ_g) fragment of the photolysis of ozone at 14 wavelengths between 287.57 and 331.52nm have been measured by time-of-flight spectroscopy. Two identical tunable dye lasers were employed, the first to photolysis ozone and the second to form O₂⁺ ions from the nascent O₂(a¹Δ_g, v,J) fragment by a 2+1 REMPI process. The ions were produced in the source region of a modified Wiley-McLaren TOF mass spectrometer, and were detected as a function of time following the REMPI pulse. The fields in the spectrometer were chosen to allow the velocities of the neutral O₂(a¹Δ_g) fragments to be determined from their flight time profiles.

At wavelengths up to 308nm, the profiles observed were those expected from spin allowed prompt dissociation of the excited molecule following absorption in a predominantly parallel transition, in agreement with previous measurements in the Hartley band. Between 308 and 318nm, wavelengths which span the thermodynamic threshold for formation of excited singlet molecular O₂(a¹Δ_g) and atomic O(¹D₂) products at 310nm, the spin allowed dissociation of vibrationally excited ozone is observed to dominate the formation of singlet molecular oxygen. Photolysis at longer wavelengths produces fragments with far higher kinetic energies, consistent with the formation of the O₂(a¹Δ_g) fragment together with ground state O(³P) atoms in a spin forbidden process.

EIGHTH EUROPEAN WORKSHOP

**POSTER
SESSION B**

Natural Alignment of Diatomic Molecules in Supersonic Seeded Beams:
Use for the Determination of Van Der Waals Intermolecular forces.

V.Aquilanti, D. Ascenzi, D. Cappelletti, R. Fedeli, and F. Pirani.

Dipartimento di Chimica dell' Università 06123 Perugia, Italy.

The characterization of spatial aspects in molecular dynamics has long been recognized as basic to the understanding of steric effects in chemical reactions, and to the assessment of the role of anisotropic forces governing collisions in the gas phase and at surfaces. One of the simplest and most general method is the collisional alignment in supersonic seeded beams: the 'seeding' phenomenon associated with the supersonic expansion of a gaseous mixtures into vacuum leads to cooling of molecular degrees of freedom and also to spatial alignment. We demonstrate for oxygen molecules that the phenomenon naturally leads to extreme quantum conditions, *i.e.* exclusive population of the ground roto-vibrational triplet state, and strong alignment monitored by a Stern-Gerlach magnetic deflection technique ¹. The important observation is made ^{2,3} that the latter depends on the final speed, so that, within the same beam, molecules traveling faster show much greater alignment than slow ones.

Measurements are reported for the scattering ⁴ of molecular oxygen both with a hot rotational energy distribution and cooled at its ground rotational state with a controlled alignment of the rotational angular momentum. The cooling and control of the alignment are achieved using supersonic expansion in beams of molecular oxygen seeded in various mixtures of Ne, He and H₂. It is shown by the integral scattering cross section with Xe and Kr in the glory energy range that information can be obtained on the isotropic and anisotropic components of intermolecular van der Waals interactions; further scattering experiments are in progress for the O₂-O₂ system and also with nitrogen molecules emerging from supersonic seeded expansions to extend the knowledge of the intermolecular anisotropies and to confirm the generality of the collisional alignment phenomenon.

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FORMATION AND DECAY OF SMALL RARE-GAS IONIC CLUSTERS

A. Bastida, X. Gadéa, N. Halberstadt, and J. Alberto BESWICK
Université de Toulouse, France

Rare-gas ionic clusters are good model systems to study size-selected properties such as photon absorption spectra, fragmentation, reaction dynamics and solvation.¹ The clusters are usually formed by electron or photon bombardment of neutral clusters generated in a supersonic expansion. A current basic question in the context of mass spectrometry techniques, is the elucidation of the fragmentation mechanisms following ionization of the neutral clusters.²

We shall report on recent simulations of formation and decay of small rare-gas clusters. The initial state is assumed to correspond to a neutral cluster in its ground electronic state and its dynamics is treated classically. Upon electron or photon excitation, the system is assumed to be vertically ionized into the manifold of coupled electronic energy surfaces of the cluster ion. These surfaces are calculated using the Diatomics In Molecules (DIM) approximation plus polarization interactions.³ This allows to take into account the effects of dipole-dipole interactions, hole delocalisation, and static and dynamic polarization of neutral atoms by the instantaneous field of the hole.

The dynamics of fragmentation are then studied using a hybrid quantum/classical technique (HWD: Hemiquantum Dynamics with the whole DIM basis).³ In this treatment, the electronic problem is handled through the evolution in time of a wave packet while the nuclear dynamics is treated classically. It presents several attractive features: i) all channel states are included; ii) the electronic basis consists of essentially local wavefunctions which may be considered a quasi-diabatic; iii) no diagonalisation of the electronic Hamiltonian is needed.

In this talk these theoretical techniques will be presented and results for Ar₃⁺ and Ar₄⁺ will be discussed and compared with experiments.^{2,4-6}

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INTENSE FEMTOSECOND LASER PULSES APPLIED TO THE MULTIPHOTON IONIZATION AND FRAGMENTATION OF MOLECULES

A. Assion, T. Baumert, V. Seyfried, R. Thalweiser, V. Weiss and G. Gerber

Universität Würzburg, Physikalisches Institut, Am Hubland, D-97074 Würzburg

By the development of ultrafast laser sources with their inherent spectral width it has become a standard technique to couple coherently quantum mechanical eigenstates. The observations of Rydberg wavepackets in atoms [1][2], showing the classical Kepler orbits of the electron around the nucleus and the observation of vibrational and rotational wavepackets in molecules [3][4] are prominent examples.

In femtosecond pump-probe experiments on the multiphoton ionization dynamics of the sodium dimer we have analyzed the vibrational wavepacket motion on the different excited states in order to distinguish between different multiphoton ionization and fragmentation processes [4]. The results of these experiments give new input into the field of controlling chemical reactions by means of time resolved laser techniques.

In experiments with high laser intensities (10^{12} W/cm²) the electronic states participating in the multiphoton ionization processes are coupled coherently in a Rabi type process. Thus populations in different electronic states are changed in a controlled manner. In this context a ground state vibrational wavepacket was generated and detected in the transient ionization signal [5]. The coherent coupling of the electronic states as a function of laser intensity is expected to influence the total ionization yield as well as the kinetic energy of the ejected photo electrons.

In additional experiments the spreading and recurrence of a vibrational wavepacket in an electronically excited state was measured and compared to quantum calculations [6][7].

Higher dimensional wavepacket motions have been observed in femtosecond time resolved experiments on the sodium trimer and sodium clusters. All the experiments described are reviewed in two recent articles [8][9].

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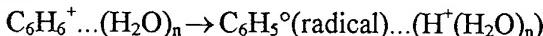
Reactions in Benzene⁺- Water clusters : evidence of a size effect for aromatic cation deprotonation

A.Courty, I.Dimicoli, J. Le Calvé and M.Mons.

*CEA, Centre d'Etudes de Saclay, Service des Photons, Atomes et Molécules, Bât 522,
91191 Gif-sur-Yvette Cedex, France*

Previous studies on the benzene-water clusters established their structure: a water cluster with a benzene (Bz) onto the surface, but did not indicate any reactivity neither in the neutral nor the ionic small clusters ($n \leq 7$). Nevertheless, the Bz^+ cation is known to have acidic properties in the condensed phase ($pK_a = -3$). This kind of system is thus expected to be an interesting model to investigate size effects in proton transfer reactions.

Benzene-water clusters are produced in a pulsed supersonic beam. The aromatic cations are formed by resonant two-photon ionization of the solvated benzene molecules. The cluster ions are then detected by TOF mass spectrometry. A typical mass spectrum, only composed of the $Bz^+-(H_2O)_n$ mass series (see figure), clearly exhibits two large intensity anomalies (magic numbers) at $n=21$ and at $n=28$. By investigating the cluster ion dynamics, these anomalies could be assigned to the evaporation of water molecules on the microsecond time scale. These characteristics are very similar to those of the protonated water clusters, in which magic numbers occur at the same sizes and have been assigned to compact structures composed of a protonated core (H_3O^+ or $H_3O^+ H_2O$) encaged in a complete shell of water molecules. This similarity strongly suggests that in large clusters ($n \geq 21$) proton transfer takes place according to the reaction:

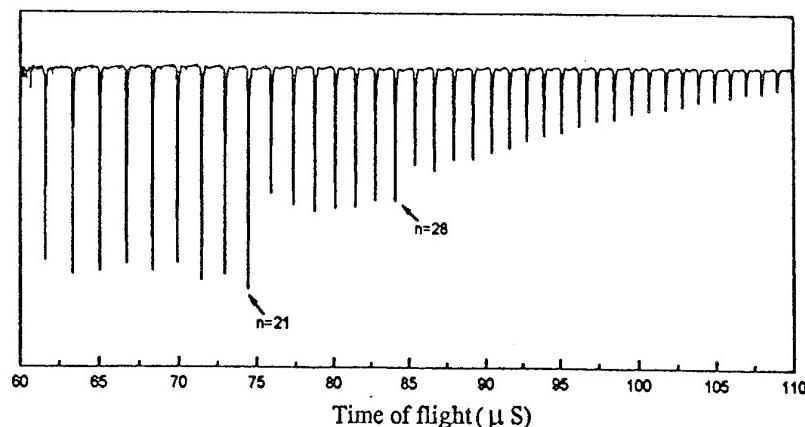


followed by successive evaporations of solvent moieties due to the exothermicity of the reaction.

The present work shows that magic numbers can be considered as a useful indication of proton transfer, especially when the exothermicity of the reaction is not large enough to separate the reaction products: the phenyl radical is found to remain on the surface of the cluster even in the case with a compact solvent shell. These results have been confirmed by a similar study with a still stronger acid, the toluene cation, which leads to the same magic numbers as in the case of benzene.

Finally this experiment illustrates the existence of a significant size effect: even in the case of a strong acid, several tens of molecules are needed in the cluster for the cation deprotonation to occur.

Mass spectrum
of $(Bz^+)(H_2O)_n$ clusters
in the $n=13-50$ size range



TIME-RESOLVED SPECTROSCOPY OF ATP IN AQUEOUS SOLUTION

S. Fu, P. Hart, and M. Daniels
Chemistry Department
Oregon State University, Corvallis
OR 97331, U.S.A.

ATP (adenyl triphosphate) is involved in several major biological processes. As a carrier of one of a major genetic component of nucleic acids, it plays a major role in replication and transcription of DNA and it is a vital component of cellular metabolic processes. The spectroscopic and photophysical behaviour of the adenyl chromophore is important for understanding the photon absorption in NA, the subsequent energy migration and localization in photochemical charge, and thus, the eventual expression in photobiological effect of solar UV.

Previous picosecond investigations have produced discordant results. Time-correlated single photon counting with a resolution of 40 ps gave resolved lifetimes of 290 ps and 4.17 ns for ATP (Rigler et al 1984); a unimodal spectrum, λ_{\max} 400nm was observed. The streak camera technique (50 ps resolution) gives both lifetimes and time-resolved spectra and Yamashita et al (1987) extracted lifetimes of 5 ps at 340 nm and 330 ps at 380 nm for 9-methyladenine. The present work has been carried out using gated fast sampling (100 ps) and tunable laser excitation to investigate these discrepancies. Variable time delays allow the acquisition of decay profiles at various emission wavelengths. Iterative reconstruction (convolution) from the instrument response function allows the number of emitting components and their lifetimes to be estimated. Spectral scanning at different delay times gives time-windowed spectra from which time-resolved spectra of the components may be obtained, based on their lifetimes.

At pH 7 we observe a two-component emission, comprising: (i) a predominant fast component with a lifetime beyond the resolution of our instrument ($\tau_1 < 100$ ps) and a spectrum with $\lambda_{\max} = 310$ nm; and (ii) a weak, slower species, $\tau_2 = 2.5$ ns with λ_{\max} at 390 nm. The spectrum of the slow component is independent of acidity (to pH 1.1) although its lifetime changes to 4.4 ns. The spectrum of the fast component progressively shifts to the red with increase in acidity. Effects of concentration and excitation wavelength will be presented and correlated with the results of Rigler and Yamashita and the structure of the solution.

DISSOCIATION OF THE OCS⁺ ION IN THE A-X FRANCK-CONDON
GAP AND IN THE A, B STATES. EXPERIMENT AND THEORY.

M.-J. Hubin-Franskin (a,[†]), J. Delwiche (b), P.-M. Guyon (c),

M. Viard-Richard (d), M. Lavollée (e), O. Dutuit (f),

J.-M. Robbe and J.-P. Flament (g)

- (a) Université de Liège, Laboratoire de Spectroscopie d'Électrons diffusés, Institut de Chimie, B6, Sart Tilman par B-4000 Liège 1, Belgium.
- (b) Université de Liège, Laboratoire de Spectroscopie de Photoélectrons , Institut de Chimie, B6, Sart Tilman par B-4000 Liège 1, Belgium.
- (c) Université de Paris-Sud, Laboratoire des Collisions Atomiques et Moléculaires (LCAM), Bât. 351, F-91405, Orsay Cedex, France.
- (d) Université Paul Sabatier, Toulouse, France.
- (e) L.U.R.E., Centre Universitaire de Paris-Sud, F-91405 Orsay, France.
- (f) Laboratoire de Physico-Chimie des Rayonnements, Bât. 350 F-91405 Orsay, Cédex, France.
- (g) Laboratoire de Dynamique Moléculaire et Photonique
Université des Sciences et Techniques de Lille, F-59655 Villeneuve d'Ascq, France.

The predissociation of selected vibronic levels of the \tilde{X} , \tilde{A} , and \tilde{B} states of the OCS⁺ ions has been studied experimentally. The product state distribution in the dissociation of OCS⁺ molecular ions has been probed by photoabsorption of the synchrotron radiation in the 13.5 to 16.5 eV energy range and threshold photoelectron-photoion coincidence (TPEPICO) spectroscopy.

Ab-initio calculations have been performed to model the potential energy curves of the $\tilde{X}^2\Pi$, $\tilde{A}^2\Pi$, $\tilde{B}^2\Sigma^+$ electronic states and also of the lowest energy $4\Sigma^-$ state. This latter is confirmed to be responsible of the predissociation in the $\tilde{A}-\tilde{X}$ Franck-Condon gap and of the $\tilde{A}^2\Pi$ state in its lowest vibrational levels. Predissociation of the B state is also discussed.

The predissociation mechanism is not statistical and favors the production of highly excited products i.e. electronically S⁺ and vibrationally CO (v) with the maximum probability for the highest energy accessible levels. For the \tilde{A} state the distribution of excess energy is little dependent on the vibrational mode selection. Predissociation in the Franck-Condon gaps involves a highly effective transfer into rotational motion.

[†] "Directeur de Recherches" of the F.N.R.S. of Belgium

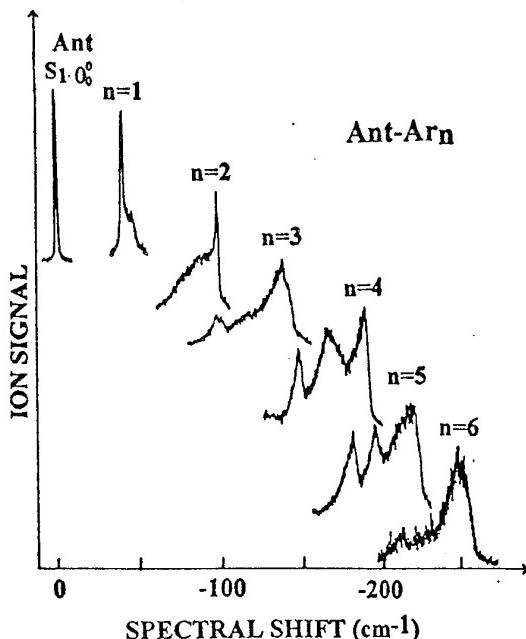
Structure and dynamics of Anthracene-Argon_n clusters (n≤6).

D. Goussu, I. Dimicoli, M. Mons, J. Le Calvé and F Piuzzi.

CEA, Centre d'Etudes Nucléaires de Saclay, Service des Photons, Atomes et Molécules, Bât. 522,
91191 Gif-sur-Yvette Cedex, France.

Van der Waals heteroclusters, consisting of an organic aromatic hydrocarbon bound to rare-gas atoms are expected to provide basic information on intermolecular interactions in large chemical systems. In the present work, van der Waals (vdW) complexes formed between anthracene (Ant) and argon (Ar) in a supersonic jet expansion have been studied using two-color, fluorescence and ionization techniques. Mass selective absorption spectroscopy was carried out by using two-color, resonant two-photon ionization (R2PI). Electronic spectra of Ant-Ar_n (n≤6) were recorded at the vicinity of the anthracene S₁←S₀ electronic origin (27687cm⁻¹) and for the vibronic transition 12̄₀ (Figure).

Two-color R2PI spectra of Ant and of Ant-Ar_n (n=1-6) vdW complexes at electronic origin.



Clear evidence for the existence of different structures for each size was found. An assignment of these structures to isomers, cold (vibrationally) and "hot" (vibrationally excited) species, is proposed. In a two-color fluorescence experiment, a hole-burning effect has been obtained for the small clusters (n≤3) indicating the existence of these species in the ground electronic state. Analysis of the size dependence of the electronic spectral shifts allows us to propose the following structures for the most abundant clusters (n≤4): 1|0, 2|0, 2|1, 2|2. In addition, field free adiabatic ionization energies have been determined for anthracene (IE=59886cm⁻¹) and all structures showing discrete bands. The ionization energy red shifts are in agreement with our structural proposals. Excited state dynamics has been studied through the determination of fluorescence life-times and two-color, R2PI time-delay spectroscopy in order to get information about the stability of the clusters. A comparison of the experimental results with intermolecular potential energy surface (PES) calculations will be presented.

SPIN-ORBIT AND ROTATIONAL AUTOIONIZATION IN HBr

N.P.L. Wales, W.J. Buma and C.A. de Lange

Laboratory for Physical Chemistry,

University of Amsterdam, Netherlands

R. Irrgang, M. Spieweck, M. Drescher, F. Gierschner
and U. Heinzmann

Fakultät für Physik, Universität Bielefeld, Germany

H. Lefebvre-Brion

Laboratoire de Photophysique Moléculaire,

Université d'Orsay, France

The rotationally resolved spin-orbit autoionization spectrum of HBr has been observed between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ionic thresholds by two different methods

- i) from the $X^1\Sigma^+$ ground state by tunable XUV light generated by resonant frequency mixing ;
- ii) from the intermediate $F^1\Delta_2$ Rydberg state by double resonant laser excitation.

The two spectra are very different which stems from the fact that (i) the $J''=0$ level is the initial state in the first experiment while the $J'=2$ level should be considered as the initial state for excitation of the Rydberg complexes in the second experiment ;

(ii) the transition moments from the initial states to the Rydberg complexes are different for the two approaches.

Using multichannel quantum defect theory (MQDT) applied to Rydberg states in an intermediate coupling case between Hund's case (a) and case (e), the assignment of the s,p,d and f Rydberg complexes can be made. From the ground state the transition to the s and d complexes are the most intense ones. From the $F^1\Delta_2$ state, there are strong transitions to f as well as d complexes and weaker transitions to the p complexes. Surprisingly, however, no s Rydberg states are observed from the latter state.

ION-PAIR FORMATION IN THE PHOTODISSOCIATION OF HF AND DF

A.J. Yencha,⁽¹⁾ A. Hopkirk,⁽²⁾ J.R. Grover,⁽³⁾ B.-M. Cheng,⁽⁴⁾ H. Lefebvre-Brion,⁽⁵⁾ and F. Keller⁽⁵⁾

⁽¹⁾ Department of Physics and Department of Chemistry, State University of New York at Albany, Albany, New York 12222
⁽²⁾ EPSRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.

⁽³⁾ Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

⁽⁴⁾ Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan, Republic of China

⁽⁵⁾ Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université Paris-Sud, 91405 Orsay CEDEX, France

The excitation functions for ion-pair formation in supersonically cooled HF and DF have been measured using synchrotron radiation with a photon resolution of 0.03 nm. The excitation functions for both molecules (see Fig. 1) are characterized by an intense, sharp peak (16.070 ± 0.002 eV and 16.131 ± 0.002 eV, respectively), essentially coincident with the thermodynamic onset for ion-pair formation, followed by weaker, broader structure to higher energy that is reminiscent of the spectral features found in ion-pair formation in HCl and DCl.¹ The measured onsets (vertical arrows in Fig. 1) at 16.032 eV for HF and 16.096 eV for DF is consistent with effective molecular rotational temperatures of 100 K and 200 K, respectively. All of the present structure is interpreted as arising from the photoexcitation of Rydberg states of the neutral molecules that are predissociated by the $V^1\Sigma^+$ ion-pair state potential. *Ab initio* calculations using multichannel quantum defect theory to include both predissociation and autoionization enabled assignments of the observed structure to be made and the construction of simulated ion-pair excitation function spectra in an energy region encompassing ~ 0.25 eV of the lowest energy part of the experimental excitation functions (see Fig. 2 for a comparison in HF). The intense first peak in the ion-pair excitation function of both molecules is assigned to a high vibrational level ($v'=17$ in HF and $v'=22$ in DF) of the 3s σ Rydberg state converging to the $A^2\Sigma^+$ ion state. Analysis of the weaker peaks immediately following this intense first peak in the excitation functions (e.g., as is shown in Fig. 2) is aided by an experimental resolution better than that of Berkowitz et al.² and by rotational cooling of the molecules and are assigned to d Rydberg complexes converging to the $v'=1$ level of both $X^2\Pi$ ion states.

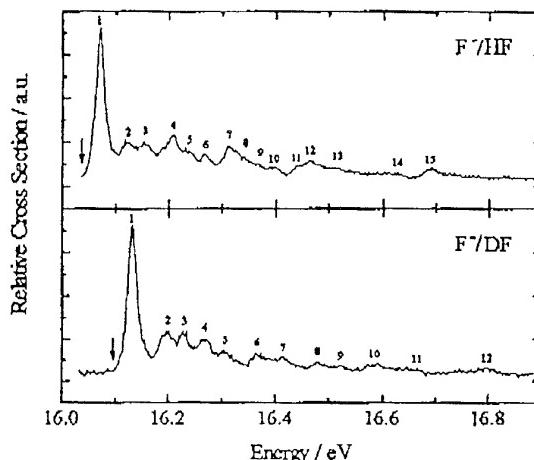


Fig. 1. Experimental excitation functions for ion-pair formation in HF and DF as obtained from the measured F signal.

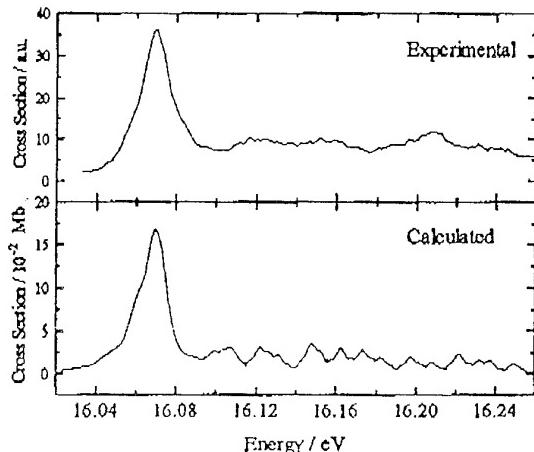


Fig. 2. Comparison of the experimental and calculated excitation function cross sections for ion-pair formation in HF.

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HIGH HARMONIC GENERATION FROM HYDROGEN ATOM IN INTENSE LASER FIELDS

Vladimir S. Melezhik ¹

Joint institute for Nuclear Research, Dubna, Moscow Region 141980, Russia

ABSTRACT

A new non-perturbative method is developed for evaluation of the high harmonic spectra generated by the hydrogen-like atoms in strong laser fields of the arbitrary polarization. The key point of this approach is a computation of the time evolution for the electron wavepacket by direct solution of the time-dependent four dimensional Schrödinger equation. The numerical scheme is based on the method of global approximation on a subspace grid for the stationary three-dimensional equation[1]. It has originally been developed for atoms in very strong electric and magnetic fields arbitrarily oriented to one another[2] and applied recently to highly excited states of an atom perturbed by an inhomogeneous field[3]. Here we evaluate the high harmonic spectra of an atom subject to a very intense ($> 10^{13} \frac{W}{cm^2}$) laser. Our results are in agreement with the data existing for the limiting case of the linearly polarized laser field[4,5].

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¹e-mail: melezhik@nusun.jinr.dubna.su

ALMOST ADIABATIC SEPARATION OF ROTATION IN REACTIVE SYSTEMS. A SOLUTION OF THE FLOPPY MOLECULE PROBLEM

Russell T Pack

*Theoretical Division (T-12, MS B268)
Los Alamos National Laboratory
Los Alamos, NM 87545*

Abstract

Many reacting and some bound systems are floppy molecules; that is, they can access configurations that range all the way from oblate symmetric top through asymmetric top to prolate symmetric top rotors. Theoretical treatments and the analysis of experimental data can become extremely complicated, expensive, and obtuse. Past attempts to separate rotational from internal motions for such systems have failed catastrophically at Eckart singularities.

We propose an almost adiabatic separation of rotation in floppy systems. It is an extension of a proposal of Bowman and is able to exactly remove all Eckart singularities, handle all their geometric phases, and include the Coriolis coupling. It also provides a clear physical picture. It is hoped that it will provide results of spectroscopic or near spectroscopic accuracy. Results of tests on the floppiest system possible will be presented.

Dynamics of benzene(NH_3)_n complexes in highly excited states

W. Radloff, Th. Freudenberg, H.-H. Ritze, V. Stert, K. Weyers and F. Noack

Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie,

Rudower Chaussee 6, D-12489 Berlin, Germany

We have studied the dynamics of benzene(NH_3)_n heteroclusters upon excitation to energy levels of about 6.2 eV by pump-probe experiments with 170 fs laser pulses. At these energy levels bare benzene excited to the S_2 electronic state loses the energy by fast internal conversion whereas ammonia molecules excited to their lowest singlet state $\tilde{\Lambda}$ predissociate very fast.

Using probe photons with an energy of 3.1 eV we found for the heteroclusters a fast internal conversion with a time constant of about 100 fs as the dominating process. The time constant was derived by fitting the time dependence of ion signals determined experimentally with corresponding theoretical curves. Some contribution is observed also due to fragmentation by NH_2 separation in the excited neutral cluster states leading to protonated $\text{C}_6\text{H}_6(\text{NH}_3)_n\text{NH}_4^+$ ions upon probe photon absorption. The results are compared with the time behaviour of protonated cluster ions obtained by ionization of pure (NH_3)_n clusters in analogous experiments.

Applying in a second run of experiments probe photons with an energy of 4.65 eV upon the first very fast internal conversion we observed a nonvanishing nearly constant ion signal for longer delay times demonstrating that the complexes are relaxed to vibrationally excited levels in the S_0 or S_1 state from which ionization is possible with 4.65 eV photons. The fraction of clusters ionized on this way increases with the number n of ammonia molecules in the heteroclusters $\text{C}_6\text{H}_6(\text{NH}_3)_n$ and is relatively small for the benzene monomer. For the heteroclusters this part slowly decreases with a time constant of about 100 ps probably due to fragmentation (by NH_3 evaporation) of vibrationally highly excited complexes in the S_0 or S_1 state. The constant signals remaining for long delay times represents the signals which we have measured in corresponding experiments with ns laser pulses at nearly identical photon energies.

H₂/D₂ multiphoton ionization and dissociation in intense sub-psec laser pulses

H. Rottke, J. Ludwig, W. Sandner

Max-Born-Institut, Rudower Chaussee 6, D-12489 Berlin, Germany

Ionization/dissociation of molecular hydrogen and its ion at high laser intensities has attracted much interest during the past few years, from the experimental as well as from the theoretical side [see for example ref. 1]. At these high intensities the potential energy curves of the molecule and its ion are strongly perturbed by the electromagnetic light field, giving rise to phenomena like bond softening, light induced bound states, or above threshold dissociation.

The experiments we are doing on H₂, D₂ use laser radiation at 1053 nm and 526.5 nm with a pulse width of 0.6 psec, generated with a regeneratively amplified Ti:Sapphire laser. The radiation is focused into an ultra high vacuum chamber where it reaches a peak intensity of $\sim 5 \times 10^{14}$ Watt/cm² within the focal spot. Photoions are detected mass selectively using time of flight mass spectroscopy, electrons are detected energy and angle resolved after passage of a drift tube.

Similar to experiments published in the literature we find a dissociation fraction H⁺/(H⁺+H₂⁺), D⁺/(D⁺+D₂⁺) increasing with laser intensity, where the dissociation fraction in D₂ is always higher than that in H₂ at a given intensity at 526.5 nm and 1053 nm. But compared to the results from the literature the dissociation fraction curves are shifted to higher intensities, due to our much shorter pulse width, which leads to higher saturation intensities for the ionization and dissociation process. In this way we can follow the processes up to a much higher intensity in the pulse before saturation sets in. The dissociation fractions at 526.5 nm and 1053 nm differ only little for H₂ at equal intensities but show a quite large difference for D₂.

Photoelectron kinetic energy spectra taken at 526.5 nm show a resonance substructure. This structure may either be generated by H₂, D₂ intermediate state resonances in the H₂, D₂ photoionization process or in H(1s), D(1s) photoionization. H(1s), D(1s) are created in the dissociation process of H₂⁺, D₂⁺ formed after ionization of the parent molecules at high light intensity. Calculation of the H(1s) photoelectron spectrum at this wavelength will help to identify these resonances. Photoelectron spectra at 1053 nm excitation wavelength are nearly structureless and extend up to high electron kinetic energies. The different shape of the spectra may be explained through the dominating ionization mechanism: multiphoton absorption at 526.5 nm and tunnel-ionization at 1053 nm.

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CHARGE STABILIZATION BY RARE GAS “SOLVENTS”

Greg Scholes, Ian Gould, David Phillips and Dick Harcourt[†]

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U. K.

and [†]School of Chemistry, University of Melbourne, Parkville 3052, Australia.

The mechanism and nature of charge stabilization by solvent is a fundamental component in the understanding of photophysical processes in clusters and the condensed phase such as photoionization and charge separation. It is known that ionization potentials of aromatic “solute” molecules are shifted to lower energy in rare gas solvents [1]. This has been attributed previously to charge-induced dipole interactions, however the present work examines the problem in detail.

The solvation of a charged solute compared to a neutral solute is examined from the perspective introduced in a recent study of electronic factors in electronic energy transfer [2]; revealing that a charge “delocalization” mechanism may be operative in certain systems. High-level *ab initio* molecular orbital and STO-6G valence bond calculations are employed in concert to calculate the adiabatic ionization potentials of ethene and ethene–rare gas solvent complexes, and to elucidate the reason for the observed red-shift in the ionization potential of the latter relative to ethene. The valence bond calculations suggest that the major stabilization of the ethene⁺.Ar complex is indeed due to charge transfer interactions which, in effect, delocalize the charge.

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Vibrational Spectroscopy of Aniline Clusters in N-H Stretching Region

T. Nakanaga, F. Ito, J. Miyawaki, K. Sugawara and H. Takeo

National Institute for Advanced Interdisciplinary Research

and National Institute of Materials and Chemical Research

1-1-4 Higashi, Tsukuba 305, Japan

A combination of infrared laser excitation and REMPI-TOF mass spectrometry has been developed as sensitive vibrational spectroscopy to study the structures of clusters and intermolecular interactions in clusters. Aniline dimer gives a broad band in its UV excitation spectrum, which has not been well analyzed yet. There are two possibilities as dimer forms, a stack model (plane to plane interaction) and a hydrogen bonding model. We are trying to observe the infrared absorption spectrum of the aniline dimer to clarify its structure. In the present study the infrared spectrum of aniline-argon cluster in the N-H stretching vibration region ($\approx 3 \mu\text{m}$) has also been observed and analyzed to derive its structure.

Aniline clusters, produced by supersonic expansion of a mixture containing aniline vapor at room temperature and argon gas with backing pressure of 1 bar, were ionized by a REMPI method using a pulsed UV laser at around 300 nm and detected with a linear TOF mass spectrometer. By adjusting UV laser frequency we could detect each neutral cluster species with high selectivity. The cluster beam was irradiated with a pulsed infrared laser (difference frequency generation, $\approx 1 \text{ mJ pulse}^{-1}$) just before the irradiation with a UV laser pulse. If the clusters absorb the infrared laser light, population in the ground vibrational state decreases, resulting in the decrease of ion signals. This depletion corresponds to infrared absorption of neutral clusters which give the ions. By changing infrared laser frequency we could obtain infrared absorption spectrum of aniline-argon cluster. The frequencies of two N-H stretching vibrations of the cluster were found to be almost the same as those of aniline monomer (only 0.5 cm^{-1} red shifted), indicating that the NH bond in the aniline-argon cluster is not affected by argon.

A Simple Recursion Polynomial Expansion of the Green's Function with Absorbing Boundary Conditions. Application to the Scattering Problem.

Vladimir A. Mandelshtam and Howard S. Taylor

Department of Chemistry, University of Southern California
Los Angeles, California 90089-0482

ABSTRACT

The basic problem in most scattering calculations is the solution of the system of linear equations $(E - H)\psi = \chi$, where the r.h.s. χ depends on particular method of solving the scattering problem. When the system is too large requiring too large a basis set, then the direct inversion of $E - H$ is not feasible. In such a case iterative methods of solving large sets of linear equations are preferred.

We show how the problem can be solved iteratively using the new recursion polynomial expansion of the ABC (absorbing boundary conditions) Green's function, $G^+(E) = [E - (H + \Gamma)]^{-1}$, where the complex optical potential Γ is used to reduce the size of the basis set needed to adequately represent the continuous dynamics of the system. The typical problem of estimating the spectral domain of the non-Hermitian operation $H + \Gamma$ to assure the stability of the polynomials is here avoided. This makes the numerical algorithm very easy to implement.

The Green's function expansion is global in energy, the energy dependence being given by simple analytic coefficients. Therefore results at many energies can be produced simultaneously from essentially a single iterative procedure.

Formal use of the energy-to-time Fourier Transform to the ABC Green's Function leads to a recursion polynomial expansion of the ABC time evolution operator which is also global in time.

Several applications of the method are considered, namely the calculation of the S matrix, reaction rates, and resonances. The new iterative approach should be of a great use in the area of the scattering calculations as well as in other related fields.

FORMATION OF MOLECULAR OXYGEN CLUSTER ANIONS IN AN
EXCIMER LASER-ABLATED (308 nm) FULLERENE SOURCE

Shihe Yang, Wenyun Lu, and Rongbin Huang

Department of Chemistry
The Hong Kong University of Science & Technology
Clear Water Bay, Kowloon, Hong Kong

The reaction of molecular oxygen clusters with laser-ablated (308 nm) hot fullerenes was studied in a molecular beam/time-of-flight mass spectrometer. Molecular oxygen cluster anions (O_2)_n⁻ were efficiently produced with n ranging from 1 to 15. The cluster anion formation is mainly attributed to the electron transfer from hot fullerenes (perhaps the fullerene molecular Rydberg states) to the oxygen clusters. Reaction of oxygen with fullerenes also resulted in the formation of small carbon cluster anions (n=3-20) and C₆₀O⁻, C₅₈O⁻, C₇₀O⁻, and C₆₈O⁻. Among the fullerene oxide anions formed, C₅₈O⁻ and C₆₈O⁻ were dominant O₂⁻ was shown to activate the fullerene disintegration to form small carbon cluster anions.

EIGHTH EUROPEAN WORKSHOP

LIST OF PARTICIPANTS

AGUILAR-NAVARRO, Antonio
Departament de Quimica Fisica
Facultat de Quimica
Marti i Franques, 1
08028 BARCELONA
Spain

AOIZ, Javier
Dpto. Quimica Fisica
Universidad Complutense Madrid
28040 MADRID
Spain

AQUILANTI, Vincenzo
Dipartimento di Chimica
Universita di Perugia
06100 PERUGIA
Italy

ASCENZI, Daniela
Dipartimento di Chimica
Universita di Perugia
Via Elce di Sotto, 8
06123 PERUGIA
Italy

ASHFOLD, Mike
School of Chemistry
University of Bristol
Cantock's Close
BRISTOL BS8 1TS
UK

BAIN, Colin
Physical & Theoretical Chemistry Lab.
University of Oxford
South Parks Road
OXFORD OX1 3QZ
UK

BASTIDA, Adolfo
LCAR-IRSAMC
Universite Paul Sabatier
118 Route de Narbonne
31062 TOULOUSE Cedex
France

BAUMERT, Thomas
Universitaet Wuerzburg
Experimentalphysik 1
Am Hubland
97074 WUERZBURG
Germany

BESWICK, Alberto
LCAR-IRSAMC
Universite Paul Sabatier
118 Route de Narbonne
31062 TOULOUSE Cedex
France

BITTO, Herbert
Physikalisch-Chemisches Institut
Universitat Zurich
Winterthurerstrasse 190
CH-8057 ZURICH
Switzerland

BOYLE, Kenneth
School of Chemistry
University of Birmingham
Edgbaston
BIRMINGHAM B15 2TT
UK

BURAK, Itamar
School of Chemistry
Tel Aviv University
69778 TEL AVIV
Israel

CHILD, Mark
Physical & Theoretical Chemistry Lab
University of Oxford
South Parks Road
OXFORD OX1 3QZ
UK

COURTY, Alexa
CEA
Centre d'Etudes de Saclay, Bat. 522
Service des Photons, Atomes et Molecules
91191 GIF-sur-YVETTE Cedex
France

DANIELS, Malcolm
Radiation Center
Oregon State University
CORVALLIS
OR 97331
USA

DELGADO-BARRIO, Gerardo
IMAFF-CSIC
Calle Serrano 113-123
28006 MADRID
Spain

DELWICHE, Jacques
Universite de Liege
Thermodynamique et Spectroscopie
Institut de Chimie - B6, Sart Tilman
B-4000 LIEGE 1
Belgium

DENZER, Wolfgang
Department of Chemistry
University of Nottingham
NOTTINGHAM NG7 2RD
UK

ELAND, John
Physical & Theoretical Chemistry Lab.
South Parks Road,
OXFORD OX1 3QZ
UK

ENRIQUEZ, Pedro
Departamento de Quimica
Universidad de La Rioja
Calle del Obispo Bustamante 3
26001 LOGRONO
Spain

FELKER, Peter
Department of Chemistry
University of California
LOS ANGELES
CA 90095-1569
USA

FERREIRA, Luis
Dpt. Fisica - Faculdade de Ciencias
Universidade de Lisboa
Campo Grande
1700 LISBOA
Portugal

FIELD, David
School of Chemistry
University of Bristol
Cantock's Close
BRISTOL BS8 1TS
UK

FRIEDRICH, Bretislav
Department of Chemistry
Harvard University
12 Oxford Street
CAMBRIDGE
MA 02138
USA

GONZALEZ, Miguel
Departamento de Quimica Fisica
Universidad de Barcelona
Marti i Franques 1
08028 BARCELONA
Spain

GORDON, Robert
University of Illinois at Chicago
Department of Chemistry (m/c 111)
845 W. Taylor Street
CHICAGO
IL 60607-7061
USA

GOUSSU, D.
CEA Centre d'Etudes de Saclay
Bat. 522
Service des Photons, Atomes et Molecules
91191 GIF-sur-YVETTE Cedex
France

GUYOT-SIONNEST, Philippe
The James Franck Institute
University of Chicago
5640 Ellis Avenue
CHICAGO
IL 60637
USA

HANCOCK, Gus
Physical & Theoretical Chemistry Lab.
University of Oxford
South Parks Road
OXFORD OX1 3QZ
UK

HEISER, Franz
Fritz-Haber-Institut
der Max-Planck-Gesellschaft
Faradayweg 4-6
D-14195 BERLIN
Germany

HERRERO, Victor
Estructura de la Materia (CSIC)
c/Serrano 123
28006 MADRID
Spain

HUBIN-FRANSKIN, Marie-Jeanne
Laboratoire de Spectroscopie
d'Electrons Diffusés
Université de Liège
Bat. B6c, Sart Tilman
B-4000 LIEGE 1
Belgium

HUTCHINSON, Henry
Blackett Laboratory
Imperial College
Prince Consort Road
LONDON SW7 2BZ
UK

von ISSENDORFF, Bernd
School of Physics & Space Research
University of Birmingham
Edgbaston
BIRMINGHAM B15 2TT
UK

JOUVET, Christophe
Lab. de Photophysique
Moléculaire de CRNS
Bat. 213
Université de Paris Sud
91405 ORSAY Cedex
France

KADODWALA, Malcolm
FOM Institute for Atomic & Mol. Physics
Kruislaan 407
1098 SJ AMSTERDAM
The Netherlands

KLUG, David
Centre for Photomolecular Sciences
Departments of Chem. & Biochemistry
Imperial College
LONDON SW7 2AY
UK

KNOESTER, Jasper
Theoretical Physics
University of Groningen
Nijenborgh 4
9747 AG GRONINGEN
The Netherlands

KUPPERMANN, Aron
Department of Chemistry
MS 127-72
California Institute of Technology
PASADENA
CA 91125
USA

de LANGE, C.A.
Laboratory of Physical Chemistry
University of Amsterdam
Nieuwe Achtergracht 127
1018 WS AMSTERDAM
The Netherlands

LEFEBVRE-BRION, Hélène
Laboratoire de Photophysique Moléculaire
Université de Paris Sud
Bat. 213
91405 ORSAY Cedex
France

LIGHT, John
Department of Chemistry
University of Chicago
5735 S. Ellis Avenue
Chicago
IL 60637
USA

MAIER, John
Institute of Physical Chemistry
University of Basel
Klingelbergstrasse 80
CH-4056 BASEL
Switzerland

MANOLOPOULOS, David
Department of Chemistry
University of Nottingham,
NOTTINGHAM NG7 2RD
UK

MELEZHIK, Vladimir
Joint Institute for Nuclear Research
Dubna
MOSCOW Region 141980
Russia

MIKHAYLICHENKO, Katia
Department of Chemistry
University of Southern California
LOS ANGELES
CA 90089-0482
USA

NOTARIO-MOLINA, Alberto
Departamento de Quimica Fisica
Universidad de Castilla La Mancha
Campus Universitario
13071 CIUDAD REAL
Spain

PACK, Russell
T-12, MS-B268
Los Alamos National Laboratory
LOS ALAMOS
NM 87545
USA

PENENT, Francis
Laboratoire de Dynamique Moleculaire
et Atomique
Universite Pierre et Marie Curie
T12-ES, Boite 75
4 Place Jussieu
75252 PARIS Cedex 05
France

PIUZZI, Francois
CEA Centre d'Etudes de Saclay
Bat. 522
Service des Photons, Atomes et Molecules
91191 GIF-sur-YVETTE Cedex
France

RADLOFF, Wolfgang
Max-Born-Institut fur Nichtlineare
Optik und Kurzzeitspektroskopie
Rudower Chaussee 6
D-12489 BERLIN
Germany

ROSTAS, Francois
Observatoire de Paris-Meudon
92195 MEUDON Cedex
France

ROSTAS, Joelle
Observatoire de Paris-Meudon
92195 MEUDON Cedex
France

ROTTKE, Horst
Max-Born Institut
Rudower Chaussee 6
D-12489 BERLIN
Germany

SCHMIDT, Jan
Department of Astronomy & Physics
Huygens Laboratory,
PO Box 9504
2300 RA LEIDEN
The Netherlands

SCHOLES, Greg
Department of Chemistry
Imperial College
LONDON SW7 2AY
UK

SCHROEDER, Jorg
Institut f. Physikalische Chemie
Universitat Gottingen
Tammannstrasse 6
D-37077 GOTTINGEN
Germany

SCHWENTNER, N.
Institut fur Experimentalphysik
Freie Universitat Berlin
Arnimallee 14
D-14195 BERLIN
Germany

SHAFIZADEH, Niloufar
Laboratoire de Photophysique Moleculaire
Bat. 213,
Universite de Paris-Sud
91405 ORSAY Cedex
France

SIMONS, John
Physical & Theoretical Chemistry Lab.
University of Oxford
South Parks Road
OXFORD OX1 3QZ
UK

SUGAWARA, Ko-ichi
National Institute for Advanced
Interdisciplinary Research
1-1-4 Higashi
TSUKUBA 305
Japan

TAYLOR, Howard
Department of Chemistry
University of Southern California
LOS ANGELES
CA 90089-0482
USA

TENNYSON, Jonathan
Physics & Astronomy Department
University College London
Gower Street
LONDON WC1E 6BT
UK

VALACHOVIC, Linda
Department of Chemistry
University of Southern California
Seaver Science Center 426
LOS ANGELES
CA 90089-0482
USA

VIGUE, Jacques
Laboratoire Collisions Agregats Reactivite
IRSAMC
Universite Paul Sabatier
118 Route de Narbonne
31062 TOULOUSE Cedex
France

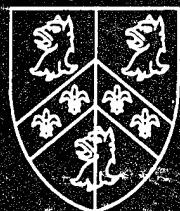
WITTIG, Curt
Department of Chemistry
University of Southern California
LOS ANGELES
CA 90089-0482
USA

YANG, Shihe
Department of Chemistry
The Hong Kong University of Science &
Technology
Clear Water Bay
KOWLOON
Hong Kong

ZARE, Richard
Department of Chemistry
Stanford University
STANFORD
CA 94305-5080
USA



MOLECULAR
SPECTROSCOPY
PHOTON
INDUCED
DYNAMICS



EIGHTH
EUROPEAN
WORKSHOP



3RD - 7TH SEPTEMBER 1995

EIGHTH EUROPEAN WORKSHOP ON MOLECULAR SPECTROSCOPY
AND PHOTON-INDUCED DYNAMICS

3rd - 7th September 1995

at

Trinity College, Oxford
The Physical and Theoretical Chemistry Laboratory
and
Rutherford Appleton Laboratory.

Final announcement and programme

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T.P. Sottley (*Oxford*)

Address for all correspondence:

8th European Workshop,
Physical and Theoretical Chemistry Laboratory,
South Parks Road,
OXFORD OX1 3QZ
U.K.

FAX: (44)-(0)-1865-275410
e-mail: jpsimons@vax.ox.ac.uk
or eland@vax.ox.ac.uk

ORGANISATION

Arrival and registration

The Workshop registration desk will be open at Trinity College on Sunday September 3rd from 6pm to 8pm, and in the foyer of the Physical and Theoretical Chemistry Laboratory (PTCL) on Monday morning, September 4th, from 9.30 am to 11 am when the meeting opens. Delegates arriving on Monday morning can go first to Trinity College to be given their rooms, then go on to the laboratory.

Accommodation and meals

All delegates, except those who have made special arrangements will be lodged in Trinity College. All meals, including the conference banquet on Thursday evening, will be taken in the College, except for lunch on Wednesday 6th at the Rutherford Appleton Laboratory. Coffee and tea will be available at the breaks in the lecture sessions. Some free drinks will accompany the poster sessions, and a bar will be available.

Travel arrangements

The conference site is easily reached by air (Heathrow or Gatwick airports), by train or by coach. There is a frequent bus service during weekdays covering the College, the Laboratory and the coach station, but all these are also within walking distance of each other.

Arrival by air. The most convenient airport is Heathrow, where there is a frequent and fast (ca. one hour) coach service (X70) to Oxford from the central bus station and from Terminal 4. The same coach also serves Gatwick at less frequent intervals. Get off in Oxford at the terminus (Gloucester Green); Trinity College is a short walk away due East along George Street and straight on at the traffic lights into Broad Street.

Arrival via London. Eurostar trains arrive in London at Waterloo station. To travel on by train, take the Underground Bakerloo line (brown on network maps) direct to Paddington station, where there are trains to Oxford. Alternatively, to travel on by coach go to the coach station at Victoria (Underground Bakerloo or Northern line to Embankment, change to Circle or District line (eastbound) to Victoria). Fast coaches (Citylink X90) leave Victoria about every twenty minutes, and arrive in Oxford at Gloucester Green, like the airport coaches (above).

Arrival in Oxford by rail. The railway station is just a bit too far from Trinity College to walk there with luggage. On Sunday take a taxi outside the station. On weekdays an electric bus (City Circle) leaves the station every ten minutes and passes Trinity College.

Social programme

The afternoon of Tuesday 5th has been set aside for individual exploration of the city or participation in organised activities.

These are:

1. Walking tours of the Colleges with amateur (mainly student) guides. Great historical erudition cannot be guaranteed, but intimate knowledge of present University life is likely.
2. Punting on the river Cherwell. This is a very pleasant and relaxing activity for a fine day. Participants will be offered the chance to take their turn with the punt pole. Informal dress is advised.

If you would like to take part in one of these activities, please register your interest with the organisers **on arrival** so that provision can be made for the numbers required.

Posters

Two poster sessions are scheduled, but there will be enough room for all the posters to be on display all the time. Each poster's owners will be asked to defend it during one session, to be notified at arrival time, but will be free to browse other posters during the other session.

The size of the poster boards is 1.2x1.2 m.

Visual aids

Two overhead transparency projectors and a standard 2x2" slide projector will be available in the lecture theatre. Please let the organisers know in good time if you want any other facilities such as video or cine projection.

Lectures

All lectures are allocated 45 minutes **including discussion**.

Please plan your oral presentation to last no longer than 35 minutes. The programme is very tight, and session chairman are expected to enforce strict time discipline.

Programme

Sunday

6-8 pm Registration at Trinity College. A buffet supper will be available from 6.30 pm.

Monday

7.45 am ***** breakfast in Trinity *****

9.30-11 Registration and coffee in the PTCL

11 am Opening ceremony-- Prof. J.P. Simons

Session 1: Photon-induced dynamics in the gas phase

Chairman: Prof. J.P. Simons

11.15 Prof. C. Wittig, "The photophysics and photochemistry of NO_3 "

12.00 Dr. J. Vigué, "Spectroscopy and photodissociation of oriented molecules"

1 pm ***** LUNCH *****

Session 2: More photon-induced dynamics

Chairman: Dr. G. Hancock

2.30 Dr. H. Bitto, "Intersystem crossing studied by high resolution
quantum beat spectroscopy"

3.15 Prof. R.J. Gordon, "Coherent control of unimolecular reactions"

4.00 ***** tea *****

4.30 Dr. D.E. Manolopoulos, "Quantum and semiclassical theories for photodissociation"

5.15 Prof. A. Kupperman, "A strong geometric phase resonance in the
 $H + D_2 = HD + D$ reaction"

6.00 Prof. M.N.R. Ashfold, "High resolution photofragment translational spectroscopy"

7.00 ***** DINNER *****

8.30 First Poster session: Group A.

Tuesday

7.45 am **** Breakfast ****

Session 3: Spectroscopy and photon-induced dynamics at interfaces

Chairman: Dr. H. Lefevre-Brion

9.00 Prof. P. Guyot-Sionnest, "Vibrational surface dynamics"

9.45 Dr. C.D. Bain, "Structure and phase transitions of monolayers of n-alcohols on water"

10.30 ***** Coffee ***

Session 4: Photon-induced processes in extraterrestrial environments

Chairman: Prof. J. Rostas

11.00 Prof. J.P. Maier, "Spectroscopy of carbon chains of relevance to astrophysics"

11.45 Dr. J. Tennyson, "Infrared observations of the impact
of comet Shoemaker-Levy-9 with Jupiter"

1 pm ***** LUNCH *****

2.30 College tours, punting etc.

7.00 ***** DINNER *****

8.30 Second Poster session-Group B

Wednesday

7.45 am **** Breakfast ****

8.45 Coaches depart for RAL

Session 5: Photon-induced processes and spectroscopy in the VUV

Chairman: Dr. J.H.D. Eland

9.15 Prof. C. deLange, "Laser photoelectron spectroscopy: chemistry with a light touch"

10.00 Dr. F. Penent, "Double photoionization processes studied by
threshold photoelectrons coincidence"

10.45 ***** Coffee ****

11.00 Dr. F. Heiser, "Fragmentation dynamics of core-excited molecules"

Session 6: Atoms and molecules in intense fields

Chairman: Dr. T.P. Softley

11.45 Dr. B. Friedrich, "Polarisation of molecules by non-resonant laser fields"

12.30 Prof. M.H.R. Hutchinson, "The interaction of atoms and molecules
with intense laser radiation"

1.15 pm ***** LUNCH *****

Wednesday (cont.)

*2.15 *Introduction to the Central Laser Facility* - Prof. Mike Key
2.45 Tour of the central laser facility

4.00 ***** tea *****
4.30 Coaches leave RAL for Oxford

7.00 ***** DINNER *****

8.30 Bar open for informal discussions

Thursday

7.45 am ***** Breakfast *****

Session 7: Spectroscopy and dynamics in van der Waals complexes and clusters

Chairman: Dr. M. Gonzalez

9.00 Dr. P.M. Felker, "Species-selective studies of intramolecular resonances
 in molecular clusters by non-linear Raman spectroscopy"
9.45 Dr. G. Delgado-Barrio, "Competitive internal transfers in metastable decay
 of cluster ions"
10.30 ***** coffee *****
11.00 Dr. C. Jouvet, "Time evolution in van der Waals reactive clusters"
11.45 Dr. B. von Issendorff, "Optical spectroscopy of ionized rare gas clusters"
1 pm ***** LUNCH *****

Session 8: Photon-induced processes and molecular spectroscopy in condensed phases

Chairman: Prof. A. Beswick

2.30 Prof. J. Schmidt, "Single molecule magnetic resonance spectroscopy"
3.15 Prof. J. Knoester, "Collective optical properties of molecular assemblies"
4.00 ***** tea *****
4.30 Dr. N. Schwentner, "Towards an understanding of elementary photochemical reactions
 in condensed phases"
5.15 Dr. D. Klug, "Relaxation dynamics in proteins studied by ultrafast spectroscopy"

6.00 *Closing remarks* - Prof. V. Aquilanti.

7.30 ***** CONFERENCE BANQUET *****